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(54) RADIATION-CURABLE COMPOSITION FOR FORMING OPTICAL WAVEGUIDE, OPTICAL WAVEGUIDE AND METHOD FOR MANUFACTURING THE SAME

(57)Abstract:

PROBLEM TO BE SOLVED: To provide an optical waveguide excellent in transmission properties and long-term stability of the properties and to provide a method for manufacturing the optical waveguide.

SOLUTION: In the optical waveguide comprising a lower clad layer, a core portion and an upper clad layer, at least one selected from the lower clad layer, the core portion and the upper clad layer is a cured body of a radiation-curable composition comprising (A) a copolymer (having alkali solubility) comprising (a) (5-50 wt.% component comprising) a radical polymerizable compound having a carboxy group, (b) (15-60 wt.% component comprising) a radical polymerizable compound having no carboxy group and (c) (5-80 wt.% component comprising) another radical polymerizable compound, (B) a compound having two or more polymerizable reactive groups per molecule and (C) a radiation polymerization initiator.

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CLAIMS

[Claim(s)]

[Claim 1] (A) The structural unit originating in the radical polymerization nature compound which has the (a) carboxyl group, (b) The structural unit originating in the radical polymerization nature compound which has an annular alkyl group and does not have a carboxyl group, And the radiation-curing nature constituent for optical waveguide formation characterized by containing the copolymer which has a structural unit originating in (c) above (a) and radical polymerization nature compounds other than (b), the compound which has two or more polymerization sexual response radicals in the (B) molecule, and (C) radiation polymerization initiator.

[Claim 2] (B) The radiation-curing nature constituent for optical waveguide formation according to claim 1 with which the polymerization sexual response radical of a component is characterized by being an ethylene nature partial saturation radical.

[Claim 3] (D) The radiation-curing nature constituent for optical waveguide formation according to claim 1 characterized by containing an organic solvent further as a component.

[Claim 4] Optical waveguide characterized by at least one of a cladding layer and the core parts consisting of a hardened material of the radiation-curing nature constituent containing a (following A) – (C) component.

(A) (Compound C) radiation-polymerization initiator which has two or more polymerization sexual response radicals in (Copolymer B) molecule which has a structural unit originating in the structural unit originating in the radical polymerization nature compound which has the structural unit and (b) annular alkyl group originating in the radical polymerization nature compound which has the (a) carboxyl group, and does not have a carboxyl group, (c) above (a), and radical polymerization nature compounds other than (b) [claim 5] Optical waveguide according to claim 4 characterized by the refractive-index difference of a cladding layer and a core part being 0.1% or more.

[Claim 6] The manufacture approach of the optical waveguide characterized by being the process in which these at least one process carries out radiation curing of the radiation-curing nature constituent according to claim 1, and forms it while including the process which forms a lower cladding layer, the process which forms a core part, and the process which forms an up cladding layer.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]**[0001]**

[Field of the Invention] This invention relates to the manufacture approach of the optical waveguide and optical waveguide which are formed using the radiation-curing nature constituent for optical waveguide formation which can form the optical waveguide which is excellent in the waveguide configuration where the purpose configuration was balanced, or a transmission characteristic, and it.

[0002]

[Description of the Prior Art] Multimedia age is greeted and optical waveguide attracts attention as a transmission medium of light from the demand of large-capacityizing of the information processing in an optical transmission system or a computer, and improvement in the speed. As such optical waveguide, quartz system waveguide is typical and, generally is manufactured according to the following processes.

** Form the lower cladding layer which consists of glass membrane by technique, such as the flame depositing method (FHD) and a CVD method, on a silicon substrate.

** Form the thin film of the minerals with which this differs from a refractive index on a lower cladding layer, and form a core part by carrying out patterning of this thin film using a reactive-ion-etching method (RIE).

** Form an up cladding layer by the flame depositing method further.

However, by such manufacture approach of quartz system waveguide, while the special manufacturing installation was required, problems, like production time starts for a long time were seen.

[0003] Then, by both developing an unexposed part as if the light of the specified quantity being irradiated and radiation curing of the predetermined location being carried out to the constituent containing the component in which radiation polymerization is possible, the artificers of this invention formed the core part etc. and have proposed the approach of manufacturing the optical waveguide which is excellent in a transmission characteristic. According to the manufacture approach of optical waveguide using such a radiation-curing nature constituent, the advantage that a short time can be manufactured only by developing negatives as compared with the manufacture approach of the conventional quartz system waveguide after irradiating the light of the specified quantity, and optical waveguide can be manufactured by low cost can be acquired. However, the case where it could be difficult to form the optical waveguide which has detailed width of face, or it could not form the optical waveguide which has the outstanding transmission characteristic even if it performs the manufacture approach of the above-mentioned optical waveguide using the radiation-curing nature constituent reported to the former was seen.

[0004]

[Problem(s) to be Solved by the Invention] This invention is made against the background of the above situations, and aims at offering the approach that the outstanding waveguide configuration, the optical waveguide which has the outstanding transmission characteristic, and such optical waveguide can be manufactured efficiently.

[0005]

[Means for Solving the Problem] The structural unit to which this invention originates in the radical polymerization nature compound which has the (A) and (a) carboxyl group, (b) The structural unit originating in the radical polymerization nature compound which has an annular alkyl group and does not have a carboxyl group, And the copolymer which has a structural unit originating in (c) above (a) and radical polymerization nature compounds other than (b) ("Copolymer (A)" is said hereafter), the compound which has two or more polymerization sexual response radicals in the (B) molecule, And the radiation-curing nature constituent for optical waveguide formation characterized by containing (C) radiation polymerization initiator The optical waveguide which formed at least one of (it may be hereafter called a "radiation-curing nature constituent"), a cladding layer, and the core parts with this constituent, and its manufacture approach are offered.

[0006]

[Embodiment of the Invention] The radiation hardenability product copolymer for optical waveguide formation (A) can be obtained by carrying out radical copolymerization of the radical polymerization nature compound which has the radical polymerization nature compound and (b) annular alkyl group which have the (a) carboxyl group, and does not have a carboxyl group, (c) above (a), and the radical polymerization nature compounds other than (b) in a solvent.

[0007] As a radical polymerization nature compound (a) which has said carboxyl group, the methacrylic-acid derivative which has a carboxyl group and ester bonds, such as dicarboxylic acid; 2-SAKUSHINO roil ethyl (meta) acrylate, such as monocarboxylic acid; maleic acids, such as an acrylic acid, a methacrylic acid, and a crotonic acid, a fumaric acid, a citraconic acid, mesaconic acid, and an itaconic acid, 2-MAREINO roil ethyl (meta) acrylate, and 2-hexahydro phthloyl ethyl (meta) acrylate, for example can be used. These compounds can be used combining independence or two sorts or more. In these, an acrylic acid, a methacrylic acid, and 2-hexahydro phthloyl ethyl (meta) acrylate are an acrylic acid and a methacrylic acid desirable still more preferably.

[0008] The rate of the structural unit originating in the radical polymerization nature compound which has the carbonyl group occupied in a copolymer (A) is 5 – 50 % of the weight, and is 10 – 40 % of the weight preferably. When it is hard coming to dissolve when this constituent is stiffened by optical exposure as the rate of this structural unit is less than 5 % of the weight, and an alkali development is performed, and it uses as a core part of optical waveguide, the core configuration as a design is not acquired and sufficient transmission characteristic is not acquired. Conversely, even if it exceeds 50 % of the weight, the thing of the configuration as a design is not obtained.

[0009] As a radical polymerization nature compound (b) which has said annular alkyl group and does not have a carbonyl group, cyclohexyl (meta) acrylate, 2-methylcyclohexyl (meta) acrylate, dicyclopentanil oxy-ethyl (meta) acrylate, isobornyl (meta) acrylate, dicyclopentanil(metha) acrylate, etc. can be mentioned, for example. These compounds can be used combining independence or two sorts or more. In these, dicyclopentanil(metha)acrylate is desirable.

[0010] The rate of the structural unit originating in the radical polymerization nature compound which has the annular alkyl group occupied in a copolymer (A), and does not have a carbonyl group is 15 – 60 % of the weight, and is 20 – 50 % of the weight preferably. The molecular weight of the copolymer obtained as this rate is less than 15 % of the weight does not fully go up, but the hardening film of this constituent of 20-micrometer or more thickness becomes difficult, and the waveguide configuration of hope cannot be produced. Conversely, if it exceeds 60 % of the weight, the solubility over the solvent of the copolymer obtained falls, and in case a copolymer is prepared, a problem will arise.

[0011] said — others — a radical polymerization nature compound (c) is used in order to mainly control the mechanical property and refractive index of a copolymer (A) moderately. As such other radical polymerization nature compounds (c), acrylic-acid (meta) alkyl ester, acrylic-acid (meta) aryl ester, dicarboxylic acid diester, aromatic series vinyl, conjugation diolefins, a nitrile group content polymerization nature compound, a chlorine content polymerization nature compound, an amide joint content polymerization nature compound, and fatty-acid vinyl can be mentioned preferably. Specifically Methyl (meta) acrylate, ethyl (meta) acrylate, Isopropyl (meta)

acrylate, n-butyl (meta) acrylate, Acrylic-acid (meta) alkyl ester, such as sec-butyl (meta) acrylate and t-butyl (meta) acrylate; Phenyl (meta) acrylate, Acrylic-acid (meta) aryl ester, such as benzyl (meta) acrylate; A diethyl maleate, Dicarboxylic acid diester, such as diethyl fumarate and itaconic-acid diethyl; Styrene, Alpha methyl styrene, m-methyl styrene, p-methyl styrene, vinyltoluene, Aromatic series vinyl, such as p-methoxy styrene; 1,3-butadiene, Conjugation diolefins, such as isoprene, 1, and 4-dimethylbutadiene Nitrile group content polymerization nature compounds, such as acrylonitrile and a methacrylonitrile; A vinyl chloride, Chlorine content polymerization nature compounds, such as a vinylidene chloride; fatty-acid vinyl [, such as amide joint content polymerization nature compound; vinyl acetate,], such as acrylamide and methacrylamide, can be used. These compounds can be used combining independence or two sorts or more, and methyl (meta) acrylate, n-butyl (meta) acrylate, styrene, especially its alpha methyl styrene, etc. are [among these] desirable. The rate of the structural unit originating in radical polymerization nature compounds other than (a) occupied in a copolymer (A) and (b) is 5 – 80 % of the weight, and is 20 – 70 % of the weight preferably.

[0012] As a polymerization solvent used in case a copolymer (A) is compounded For example, a methanol, ethanol, ethylene glycol, a diethylene glycol, Alcohols, such as propylene glycol; Cyclic ether; ethylene glycol monomethyl ether, such as a tetrahydrofuran and dioxane, Ethylene glycol monoethyl ether, ethylene glycol wood ether, Ethylene glycol diethylether, the diethylene-glycol monomethyl ether, Diethylene glycol monoethyl ether, diethylene-glycol wood ether, Diethylene-glycol diethylether, diethylene-glycol ethyl methyl ether, The alkyl ether of polyhydric alcohol, such as propylene glycol monomethyl ether and the propylene glycol monoethyl ether; Ethylene glycol ethyl ether acetate, The alkyl ether acetate of polyhydric alcohol, such as diethylene-glycol ethyl ether acetate and propylene glycol ethyl ether acetate; Toluene, Aromatic hydrocarbon, such as a xylene; An acetone, a methyl ethyl ketone, Methyl isobutyl ketone, a cyclohexanone, 4-hydroxy-4-methyl-2-pentanone, Ketones, such as diacetone alcohol; Ethyl acetate, butyl acetate, ethyl lactate, 2-hydroxy ethyl propionate, 2-hydroxy-2-methyl ethyl propionate, 2-hydroxy-2-methyl ethyl propionate, ethoxy ethyl acetate, Ester, such as hydroxyacetic acid ethyl, 2-hydroxy-3-methyl butanoic acid methyl, 3-methoxy methyl propionate, 3-methoxy ethyl propionate, 3-ethoxy ethyl propionate, and 3-ethoxy methyl propionate, is mentioned. Cyclic ether, the alkyl ether of polyhydric alcohol, the alkyl ether acetate of polyhydric alcohol, ketones, and ester are [among these] desirable.

[0013] Moreover, as a polymerization catalyst in radical copolymerization, the usual radical polymerization initiator can be used, for example, organic peroxide, such as an azo compound; benzoyl peroxide [, such as – azobis – (4-methoxy-2'-dimethylvaleronitrile)], lauroyl peroxide, t-butylperoxy pivalate, and 2 and 2(- azobisisobutyronitril, and '2, 2')-azobis – (2,4-dimethylvaleronitrile), 2, and 2 '1, 1'-screw-(t-butylperoxy) cyclohexane, a hydrogen peroxide, etc. can be mentioned. When using a peroxide for a radical polymerization initiator, it is good also as an initiator of a redox type combining a reducing agent. The desirable average molecular weight of the copolymer (A) obtained is 3,000–100,000. This molecular weight is defined by the polystyrene conversion called for by the gel permission chromatography (GPC). It becomes difficult to carry out coating of this constituent to molecular weight being less than 3,000 by predetermined thickness on a substrate. On the contrary, if molecular weight exceeds 100,000, in case optical waveguide will be formed with this constituent, the target waveguide configuration may not be acquired.

[0014] The compounds (B) which have two or more polymerization sexual response radicals in the molecule which constitutes the constituent of this invention are thermal polymerization and/or a compound to photopolymerize, and can illustrate a compound as shown below.

The compound which has two or more ethylene nature partial saturation radicals in a molecule; (meta) the compound which contains an acryloyl radical or a vinyl group in [two or more] a molecule can be used. As such a compound, for example Ethylene GURIKORUJI (meta) acrylate, Tetra-ethylene GURIKORUJI (meta) acrylate, polyethylene GURIKORUJI (meta) acrylate, To 1, 4-butane JIORUJI (meta) acrylate, 1, and 6-, KISANJIORUJI (meta) acrylate, Neopentyl GURIKORUJI (meta) acrylate, tris (2-hydroxyethyl) iso SHIANURETOJI (meta) acrylate, Bis (hydroxymethyl) tricyclo DEKANJI (meta) acrylate, The di(meth)acrylate of the diol which is the

adduct of the ethyleneoxide of bisphenol A, or propylene oxide, The di(meth)acrylate of the diol which is the adduct of the ethyleneoxide of hydrogenation bisphenol A; or propylene oxide, The epoxy (meta) acrylate which made acrylate (meta) add to the diglycidyl ether of bisphenol A, the diacrylate of polyoxyalkylene-ized bisphenol A, etc. are mentioned. As acrylate (meta) which furthermore contains three or more acryloyl (meta) radicals in a molecule The compound in which the acrylic acid (meta) three mols or more carried out the ester bond to the polyhydric alcohol which has three or more hydroxyl groups, For example, TORIMECHI roll pro pantry (meta) acrylate, pen TAERISURITORUTORI (meta) acrylate, Trimethylol propane TORIOKISHI ethyl (meta) acrylate, tris (2-hydroxy ethyl) iso SHIANURETOTORI (meta) acrylate, dipentaerythritol hexa (meta) acrylate, etc. are mentioned. Moreover, a polyether, polyester, the polyether acrylic oligomer that has a polyurethane frame, polyester acrylic oligomer, polyurethane acrylic oligomer, or poly epoxy acrylic oligomer can also be used for a principal chain.

[0015] as these commercial items — YUPIMA [] UV — SA1002 and SA2007 (above) The Mitsubishi Chemical make, screw coat #195, #230, #215, #260, #295, #300, #335H.P., # 360, #400, #540, and # — 700 and 3 — PA and GPT (above) The OSAKA ORGANIC CHEMICAL INDUSTRY make, light acrylate 4 EG-A, 9 EG-A, NP-A, DCP-A, BP-4EA, BP-4PA, PE-3A, PE-4A, DPE-6A (above, product made from the Kyoeisha chemistry), KAYARAD MANDA, HX-220, HX-620, R-551, R-712, R-604, R-684, PET-30, GPO-303, TMPTA, DPHA, D-310, D-330, DPCA-20, -30, -60, -120 (above) The Nippon Kayaku make, ARONIKKUSU M208, M210, M215, M220, M240, M305, M309, M310, M315, M325, M400, M1200, M6100, M6200, M6250, M7100, M8030, M8060, M8100, M8530, and M8560 — M9050 (above, Toagosei make), RIPOKISHI VR-77, VR-60, VR-90 (above) The Showa High Polymer make, Ebecryl 81, 83, 600, 629, 645, 745, 754, 767, 701, 755, 705, 770, 800, 805, 810, 830, 450, 1830, and 1870 (above) The product made from die cel UCB, the beam sets 575, 551B, 502H, and 102 (above, product made from the Arakawa chemistry), etc. are mentioned.

[0016] The compound which has two or more cyclic ether in a molecule; the compound which has two or more cyclic ether can be used into a molecule among an oxirane compound, an oxetane compound, an oxo-run compound, etc. For example, it is 3 and 4-epoxycyclohexyl methyl as oxirane compounds. — 3', 4'-epoxy cyclohexane carboxylate, 2-(3, 4-epoxycyclohexyl -5, 5-spiro -3, 4-epoxy) cyclohexane-metadioxane, A bis(3, 4-epoxycyclohexyl methyl) horse mackerel peat, a bis(3, 4-epoxy-6-methylcyclohexyl methyl) horse mackerel peat, 3, 4-epoxy-6-methylcyclohexyl - 3', 4' - epoxy -6'-methylcyclohexane carboxylate, Methylenabis (3, 4-epoxy cyclohexane), dicyclopentadiene diepoxyde, The JI (3, 4-epoxycyclohexyl methyl) ether of ethylene glycol, An ethylene screw (3, 4-epoxy cyclohexane carboxylate), Epoxidation tetra-benzyl alcohol, the lactone denaturation 3, 4-epoxycyclohexyl methyl - 3', 4'-epoxy cyclohexane carboxylate, Lactone denaturation epoxidation tetrahydro benzyl alcohol, cyclohexene oxide, Bisphenol A diglycidyl ether, bisphenol F diglycidyl ether, Bisphenol S diglycidyl ether, hydrogenation bisphenol A diglycidyl ether, Hydrogenation bisphenol F diglycidyl ether, hydrogenation bisphenol A D diglycidyl ether, Bromination bisphenol A diglycidyl ether, bromination bisphenol F diglycidyl ether, Bromination bisphenol S diglycidyl ether, epoxy novolak resin, 1,4-butanediol diglycidyl ether, 1, 6-hexanediol diglycidyl ether, Glycerol triglycidyl ether, trimethylolpropane triglycidyl ether, Polyethylene glycol diglycidyl ether and polypropylene glycol diglycidyl ether; Ethylene glycol, Propylene glycol, By adding one sort or two sorts or more of alkylene oxide to aliphatic series polyhydric alcohol, such as a glycerol The monoglycidyl ether of the diglycidyl ester; aliphatic series higher alcohol of the Pori glycidylethers; aliphatic series long-chain dibasic acid of the polyether polyol obtained; A phenol, The glycidyl ester of a monoglycidyl ether; higher fatty acid of the polyether alcohol which adds alkylene oxide to cresol, butylphenol, or these, and is obtained; Epoxidized soybean oil, Epoxy butyl stearate, epoxy stearin acid octyl, the epoxidation linseed oil, etc. can be mentioned. As an oxetane compound, 3, a 7-bis(3-OKISETANIRU)-5-OKISA-nonane, 3 and 3'-(1, 3-(2-MECHIRENIRU) propane diyl screw (oxy-methylene)) screw - (3-ethyl oxetane), 1, 4-bis[(3-ethyl-3-OKISETA nil methoxy) methyl] benzene, 1, 2-bis[(3-ethyl-3-OKISETA nil methoxy) methyl] ethane, 1, a 3-bis[(3-ethyl-3-OKISETA nil methoxy) methyl] propane, The ethylene glycol bis(3-ethyl-3-OKISETA nil methyl) ether, The JISHIKURO pentenyl bis(3-ethyl-3-OKISETA nil methyl) ether, The

triethylene glycol bis(3-ethyl-3-OKISETA nil methyl) ether, The tetraethylene glycol bis(3-ethyl-3-OKISETA nil methyl) ether, The tricyclodecane diyl dimethylene (3-ethyl-3-OKISETA nil methyl) ether, The trimethylol propane tris (3-ethyl-3-OKISETA nil methyl) ether, 1, 4-bis(3-ethyl-3-OKISETA nil methoxy) butane, 1, a 6-bis(3-ethyl-3-OKISETA nil methoxy) hexane, The pentaerythritol tris (3-ethyl-3-OKISETA nil methyl) ether, The pentaerythritol tetrakis (3-ethyl-3-OKISETA nil methyl) ether etc. can be illustrated, and these can be used combining independent one sort or two sorts or more.

[0017] As these commercial items, the EPO lights 40E, 100E, and 70P, 1500NP, 100MF, 4000 and 3002 (above, product made from the Kyoeisha chemistry), the SEROKI sides 2021 and 2081, GT301 and GT401, EPOLEAD CDM, PB3600, the EPO friends A1005, A1010, and A1020 (above, Daicel Chemical Industries make), DENAKORU 611, 612, 512, 521, 411, 421, 313, and 321 (above, Nagase Brothers formation make), etc. are mentioned.

[0018] Moreover, you may be the compound which contains the above mentioned ethylene nature partial saturation radical and both at least one or more reactivity radicals of cyclic ether in a molecule, respectively. For example, glycidyl (meta) acrylate, vinyl cyclohexene oxide, 4-vinyl epoxy cyclohexane, 3, and 4-epoxycyclohexyl methyl (meta) acrylate etc. is mentioned. As for these compounds (B), it is desirable to use the compound which may use by independence or two sorts or more, and contains an ethylene nature partial saturation radical in [two or more] a molecule especially. the (Copolymer A) 100 weight section — receiving — desirable — the 30 – 150 weight section — it is the 50 – 130 weight section more preferably. In case optical waveguide is formed in case of under 30 weight sections, when the target waveguide configuration may not be acquired and the 150 weight sections are exceeded, compatibility with a copolymer (A) may worsen and may produce a film dry area on a hardened material front face.

[0019] The radiation polymerization initiator (C) which constitutes the constituent of this invention is an initiator which can generate the active species which can carry out the polymerization of the compound (B) described above with the radiation. A radiation means infrared radiation, a visible ray, ultraviolet rays and an X-ray, an electron ray, alpha rays, beta rays, and ionizing radiation like a gamma ray here. Therefore, the radiation polymerization initiator which is a component (C) is needed, and a photosensitizer is added further if needed. It can divide roughly into what decomposes by optical exposure and generates a radical as a radiation polymerization initiator (radiation radical polymerization initiator), and the thing (radiation cationic initiator) which generates a cation.

[0020] As a radiation radical polymerization initiator, for example An acetophenone, acetophenone benzyl ketal, A 1-hydroxy cyclohexyl phenyl ketone, 2, and 2-dimethoxy-2-phenyl acetophenone, xanthone and full — me — non and ** NZUARUDEHIDO, a fluorene, and anthraquinone — A triphenylamine, a carbazole, 3-methylacetophenone, 4-chlorobenzo phenon, A 4 and 4'-dimethoxy benzophenone, 4, and 4'-diamino benzophenone, A Michler's ketone, the benzoin propyl ether, benzoin ethyl ether, Benzyl dimethyl ketal, 1-(4-isopropyl phenyl)-2-hydroxy-isobutane-1-ON, 2-hydroxy - 2-methyl-1-phenyl propane-1-ON, a thioxan ton, A diethyl thioxan ton, 2-isopropyl thioxan ton, 2-chloro thioxan ton, 2-methyl-1-[4-(methylthio) phenyl]-2-morpholino-propane-1-ON, 2, 4, 6-trimethyl benzoyl diphenyl phosphine oxide, and screw-(2, 6-dimethoxybenzoyl)- 2, 4, and 4-trimethyl pentyl phosphorette hydrogen oxide etc. is mentioned.

[0021] As a commercial item of a radiation radical polymerization initiator, Irgacure 184, 369, 651, 500, 819, 907, 784, and 2959, CGI1700, CGI1750, CGI11850 and CG 24-61, Darocurl 116 and 1173 (above, made in Tiba Speciality Chemicals), LucirinTPO, TPO-L (above, BASF make), YUBEKURIRU P36 (product made from UCB), etc. are mentioned, for example.

[0022] The onium salt which has the structure expressed with the following general formula (1) as a radiation cationic initiator can be mentioned. This onium salt is a compound which emits Lewis acid by receiving light.

[R12a R13b R14c R15d W]+m[MXn+m]-m (1)

It is that R12, R13, R14, and R15 are the same or a different organic radical, and a cation is onium ion among [type and (a+b+c+d) is [W is S, Se, Te, P As, Sb Bi, O, I, Br, Cl, or N**N, and / a, b, c, and d are the integers of 0-3, respectively, and] equal to the valence of W. M is the

metal or metalloid which constitutes the neutral atom of a halogenide complex $[MX_{n+m}]$, for example, is B, P, As, Sb, Fe, Sn, Bi, aluminum, calcium, In, Ti, Zn, Sc, V, Cr, Mn, Co, etc. X is halogen atoms, such as F, Cl, and Br, m is the charge of the net of halogenide complex ion, and n is the valence of M.]

In a general formula (1) as an example of onium ion Diphenyliodonium, 4-methoxy diphenyliodonium, bis(4-methylphenyl) iodonium, Bis(4-tert-butylphenyl) iodonium, bis(dodecyl phenyl) iodonium, Triphenylsulfonium, diphenyl-4-thio phenoxyphenyl sulfonium, A bis[4-(diphenyl SURUFONIO)-phenyl] sulfide, a bis[4-(JI (4-(2-hydroxyethyl) phenyl) SURUHONIO)-phenyl] sulfide, eta₅-2 and 4-(cyclo pen TAJIENIRU) [1, 2, 3, 4, 5, and 6-eta-(methylethyl)-benzene]-iron (1+) etc. is mentioned.

[0023] As an example of the anion (MX_{n+m}) in the above-mentioned general formula (1), tetrafluoroborate (BF_4^-), hexafluorophosphate (PF_6^-), hexafluoroantimonate (SbF_6^-), hexafluoroarsenate (AsF_6^-), hexa chloro antimonate ($SbCl_6^-$), etc. are mentioned. As onium salt which can be used as a radiation cationic initiator, it sets to said general formula (27), and is general formula: $[MX_n(OH)^{-}]$ instead of $[MX_{n+m}]$.

(— here, M, X, and n are as a definition about a general formula (1).) — the onium salt which has other anions, such as the anion expressed, perchloric acid ion (ClO_4^-), trifluoro methysulfonic acid ion ($CF_3SO_3^-$), fluorosulfonic acid ion (FSO_3^-), toluenesulfonic acid ion, trinitrobenzene sulfonic acid ion, and trinitrotoluene sulfonic acid ion, is mentioned.

[0024] As a commercial item of a radiation cationic initiator For example, UVI-6950, UVI-6970, UVI-6974, UVI-6990 (above) Union Carbide, ADEKAOPUTOMA SP-150, SP-151, SP-170, SP-171 (above) Asahi Denka Kogyo K.K., Irgacure 261 (above, Ciba-Geigy), CI-2481, CI-2624, CI-2639, CI-2064 (above) Nippon Soda Co., Ltd., CD-1010, CD-1011, CD-1012 (above) Sartomer, DTS-102, DTS-103, NAT-103, NDS-103, TPS-102, TPS-103, MDS-103, MPI-103, BBI-101, BBI-102, BBI-103 (above) Green Chemistry, Degacure K126 (Degussa AG make) etc. is mentioned. The aforementioned radiation polymerization initiator can constitute the (C) component combining one-sort independence or two or more sorts of things.

[0025] When it is made into a component (A) and the total quantity 100 weight section of (B), as for the content rate of the (C) component in the radiation-curing nature constituent of this invention, it is desirable that it is usually 0.1 – 20 weight section, and it is desirable that it is especially 0.2 – 10 weight section. (C) When the content rate of a component is under the 0.1 weight section, hardening may not fully advance but may produce a problem in the transmission characteristic of optical waveguide. On the other hand, if 20 weight sections are exceeded, an initiator may have a bad influence on a long-term transmission characteristic.

[0026] Moreover, in a radiation-curing nature constituent, it is also desirable to use together with the radiation polymerization initiator mentioned above, and to blend a photosensitizer. This reason is because energy lines, such as light, can be absorbed more effectively by using a photosensitizer together. as such a photosensitizer — derivative [of a thioxan ton, a diethyl thioxan ton, and a thioxan ton]; — a derivative; coumarin, a keto coumarin, etc. of the derivative; xanthone of the derivative; anthracene of anthraquinone, bromine anthraquinone, and anthraquinone, a bromine anthracene, anthracene derivative; perylene, and perylene, a thioxan ton, and a thioxan ton can be mentioned. These photosensitizers need to choose the sensitizer for which it was suitable according to the class of initiator.

[0027] In the radiation-curing nature constituent of this invention, in the range which does not spoil the property of the radiation-curing nature constituent of this invention if needed other than the aforementioned component For example, the compound and macromolecule resin which contain one polymerization sexual response radical in a molecule, For example, an epoxy resin, acrylic resin, polyamide resin, polyamidoimide resin, Polyurethane resin, a polybutadiene resin, polychloroprene resin, polyether resin, Polyester resin, a styrene-butadiene block copolymer, petroleum resin, xylene resin, ketone resin, cellulosic resin, a fluorine system polymer, and a silicone system polymer polymer can be blended.

[0028] An antioxidant, an ultraviolet ray absorbent, light stabilizer, a silane coupling agent, a painted-surface amelioration agent, thermal polymerization inhibitor, a leveling agent, a surfactant, a coloring agent, a preservation stabilizer, a plasticizer, lubricant, a filler, a particle, an

antioxidant, a wettability amelioration agent, an antistatic agent, etc. can be blended as various additives further again if needed in addition to the above-mentioned component. Here, as an antioxidant, it is Irganox 1010, 1035, 1076, and 1222 (above), for example. The product made from tiba SUPESHARUTI KEMIKARUZU, Antigene P, 3C, FR, Sumi Reiser (Sumitomo Chemical make), etc. are mentioned. As an ultraviolet ray absorbent For example, Tinuvin P, 234, 320, 326, 327, 328, 329, 213 (above) The product made from tiba SUPESHARUTI KEMIKARUZU, Seesorb 102, 103, 110, 501, 202, 712, and 704 (above, SHIPRO formation make), etc. are mentioned. As light stabilizer For example, Tinuvin 292, 144, 622LD (above, product made from tiba SUPESHARUTI KEMIKARUZU), SANORU [LS and Sumisorb] 770 (Sankyo make) TM-061 (Sumitomo Chemical make) etc. is mentioned. As a silane coupling agent for example, as gamma-aminopropyl triethoxysilane, gamma-mercaptopropyltrimethoxysilane, gamma-meta-acryloxypropyltrimethoxysilane, and a commercial item SH 6062 and 6030 (above, Dow Corning Toray Silicone make), KBE 903, 603, and 403 (above, Shin-Etsu Chemical make), etc. are mentioned. As a painted-surface amelioration agent For example, silicone additives, such as a dimethylsiloxane polyether, are mentioned. As a commercial item, DC-57, DC-190 (above, Dow Corning make), SH 1 28PA, SH-29PA, SH-30PA, SH-190 (above) The Dow Corning Toray Silicone make, KF351, KF352, KF353 and KF354 (above, Shin-Etsu Chemical make), L-700, L-7002, L-7500, FK-024-90 (above, Nippon Unicar make), etc. are mentioned.

[0029] As for the radiation-curing nature constituent of this invention, it is still more desirable as a (D) component to contain an organic solvent. Since suitable viscosity can be obtained while the preservation stability of a radiation-curing nature constituent improves by adding an organic solvent, the optical waveguide which has uniform thickness can be formed.

[0030] Although it can choose as a class of organic solvent in the range which does not spoil the purpose of this invention, and effectiveness, it is usually desirable that the boiling point under atmospheric pressure is the organic compound which has a value within the limits which are 50–200 degrees C, and it is the organic compound made to dissolve each constituent in homogeneity. The organic solvent specifically used in case the copolymer of a component (A) is prepared can be used. As a desirable organic solvent, alcohols, ester, and ketones are mentioned and at least one solvent chosen from the group which consists of propylene glycol monomethyl ether, ethyl lactate, methyl isobutyl ketone, methyl amyl ketone, toluene, a xylene, and a methanol is mentioned as a more desirable organic solvent.

[0031] When it is made into the AUW 100 weight section of (C) from a component (A), as for the content of an organic solvent, it is desirable to consider as the value of the 10 – 200 weight section within the limits. It is because the viscosity control of a radiation-curing nature constituent may become difficult if the addition of this organic solvent becomes under 10 weight sections, and is because it may become difficult to form the optical waveguide which has sufficient thickness if the addition of an organic solvent exceeds the 200 weight sections on the other hand.

[0032] The radiation-curing nature constituent of this invention chooses suitably the class of the above-mentioned (A) component and (B) component, loadings, etc., in order to consider as a refractive index required for the part to be used, i.e., a cladding layer, and a core part. In case the radiation-curing nature constituent of this invention is prepared, it is desirable to make the viscosity into the value within the limits of 1–10,000cps (25 degrees C), it is more desirable to consider as the value within the limits of 5–8,000cps (25 degrees C), and it is still more desirable to consider as the value within the limits of 10–5,000cps (25 degrees C).

[0033] Optical waveguide drawing 1 is the sectional view showing the fundamental configuration of the optical waveguide constituted with the application of the radiation-curing nature constituent of this invention. As shown in this drawing 1, optical waveguide is constituted including the substrate 12 extended in the direction of a right angle (the depth direction) in space, the lower cladding layer 13 formed on the front face of this substrate 12, the core part 15 which was formed on this lower cladding layer 13 and which has specific width of face, and the up cladding layer 17 formed by carrying out a laminating on the lower cladding layer 13 containing this core part 15. And as waveguide loss decreases, the core part 15 is covered with the lower cladding layer 13 and the up cladding layer 17 including the flank, and is in the condition laid

underground as a whole.

[0034] In the optical waveguide of the above configurations, although especially the thickness of a lower cladding layer, an up cladding layer, and a core part is not restricted, respectively, it is desirable to, make [lower clad layer thickness] 3–200 micrometers and up clad layer thickness into the value within the limits of 1–200 micrometers for the thickness of 1–200 micrometers and a core part for example. Moreover, although not limited especially about the width of face of a core part, either, it is desirable to consider as the value within the limits of 1–200 micrometers for example.

[0035] Moreover, it is required to make the refractive index of a core part larger than which refractive index of the lower part and an up cladding layer. Therefore, while making the refractive index of a core part into the value of 1.420–1.650 within the limits to light with a wavelength of 400–1,600nm, it is desirable to make the refractive index of a lower cladding layer and an up cladding layer into the value of 1.400–1.648 within the limits, respectively. Moreover, it is desirable that the refractive-index difference of a core part and a cladding layer is separated 0.1% or more, and it is desirable to make especially the refractive index of a core part into a value larger at least 0.1% than the refractive index of a cladding layer. As for the optical waveguide of this invention, at least one of the above-mentioned cladding layer and the core parts consists of a hardened material of the radiation-curing nature constituent of this invention. The cladding layer and core part which are not formed with the hardened material of the radiation-curing nature constituent of this invention can be formed by polyimide, polyacrylate, the polycarbonate, a polysiloxane, etc.

[0036] Optical waveguide is formed through a process as shown in drawing 2. That is, after carrying out coating of the radiation-curing nature constituent for forming those layers for each of lower cladding layers 13, core parts 15, and up cladding layers (not shown), it is desirable to form by carrying out radiation curing. In addition, the following examples of formation explain a lower cladding layer, a core part, and an up cladding layer supposing forming from the constituent for lower layers which is a radiation-curing nature constituent with which the hardened material with which refractive indexes differ after hardening, respectively is obtained, the constituent for cores, and the constituent for the upper layers. And it is desirable to use as the constituent for cores the radiation-curing nature constituent which gives the hardening film of the highest refractive index using two sorts or three sorts of radiation-curing nature constituents with which the difference of a refractive index serves as proper magnitude, and to use other radiation-curing nature constituents as the constituent for lower layers and a constituent for the upper layers. However, the constituent for lower layers and the constituent for the upper layers may be the same radiation-curing nature constituents, it is economically advantageous that it is the usually same constituent, and it is more desirable from manufacture management becoming easy.

[0037] ** As shown in preparation **** of a substrate, and drawing 2 (a), prepare the substrate 12 which has a flat front face. Especially as a class of this substrate 12, although not restricted, a silicon substrate, a glass substrate, etc. can be used, for example.

[0038] ** It is the process which forms the lower cladding layer 13 in the front face of the substrate 12 in which the lower cladding layer carried out formation process preparation. As shown in drawing 2 (b), apply the constituent for lower layers to the front face of a substrate 12, it is made to dry or prebake, and, specifically, the thin film for lower layers is formed in it. And this thin film for lower layers can be stiffened by irradiating a radiation, and the lower cladding layer 13 can be formed. In addition, it is desirable to irradiate a radiation all over a thin film and to harden the whole in the formation process of the lower cladding layer 13.

[0039] Here, as the method of application, approaches, such as a spin coat method, a dipping method, a spray method, the bar coat method, the roll coat method, the curtain coat method, gravure, the silk screen method, or the ink jet method, can be used for the constituent for lower layers. Among these, since the thin film for lower layers of uniform thickness is obtained especially, it is more desirable to adopt a spin coat method. Moreover, since the rheology property of the constituent for lower layers should be appropriately corresponded to the method of application, it is desirable to blend various leveling agents, a CHIKUSO grant agent, a filler, an

organic solvent, a surfactant, etc. if needed. Moreover, as for the thin film for lower layers which consists of a constituent for lower layers, it is desirable after spreading to prebake at the temperature of 50–200 degrees C in order to remove an organic solvent etc. In addition, they are the contents which are applied also in the formation process of the core part mentioned later, and the formation process of an up cladding layer about the method of application in the formation process of a lower cladding layer, and amelioration of a rheology property.

[0040] Moreover, although there is nothing also about the exposure of the radiation at the time of forming a lower cladding layer especially at the thing restricted, it is desirable to irradiate the radiation of 2 so that an exposure may serve as 10 – 5,000 mJ/cm², and to expose it the wavelength of 200–390nm and the illuminance of 0.1–500mW/cm. Although the light, ultraviolet rays, infrared radiation, an X-ray, alpha rays, beta rays, a gamma ray, etc. can be used here as a class of radiation irradiated, especially ultraviolet rays are desirable. And as irradiation equipment of a radiation (ultraviolet rays), it is desirable to, use a high-pressure mercury lamp, a low-pressure mercury lamp, a metal halide lamp, an excimer lamp, etc. for example. Moreover, heat-treating further (henceforth "postbake") is desirable so that the whole paint film surface may harden enough after exposure. What is necessary is to be 50–300 degrees C preferably, for example, just to usually make it into the heating conditions of for [5 minutes] – 72 hours 30–400 degrees C, although this heating condition changes according to the combination presentation of a radiation-curing nature constituent, the class of additive, etc. In addition, they are the contents which are applied also in the formation process of the core part mentioned later, and the formation process of an up cladding layer about the exposure of the radiation in the formation process of a lower cladding layer, a class, and the irradiation equipment of a radiation (ultraviolet rays).

[0041] ** it is shown on formation, next this lower cladding layer 13 of a core part at drawing 2 (c) — as — the constituent for cores — applying — desiccation — or make it prebake further and form the thin film 14 for cores. Then, as shown in drawing 2 (d), it is desirable to irradiate a radiation 16 to the top face of the thin film 14 for cores through the photo mask 19 which has the predetermined Rhine pattern according to a predetermined pattern. Since only the part where the radiation was irradiated hardens by this, as shown in drawing 2 (e), the core part 15 which consists of hardening film by which patterning was carried out can be formed on the lower cladding layer 13 by carrying out development removal of the part which is not hardened [other].

[0042] Moreover, after the exposure of the radiation 16 to the thin film 14 for cores for forming the core part 15 is performed according to the photo mask 19 which has a predetermined pattern, by developing a part for an unexposed part with a developer, an unnecessary non-hardened part is removed and the core part 15 is formed of this. Thus, the approach of a-c which it is not restricted to the approach using the photo mask which consists of the transparency section and the nontransparent section of a radiation as an approach of irradiating a radiation according to a predetermined pattern, for example, is shown below is mentioned.

- a. How to use a means to form the mask image using the same principle as a liquid crystal display which consists of a radioparity field and a radiopacity field according to a predetermined pattern in electro-optics.
- b. How to irradiate a radiation through the optical fiber corresponding to the predetermined pattern in this light guide section material using the light guide section material which comes to bundle many optical fibers.
- c. How to irradiate a radiation-curing nature constituent, while making the convergent radiation obtained according to condensing nature optical system, such as a laser beam or a lens, and a mirror, scan.

In addition, after exposure, in order to promote hardening of an exposure part, heat-treating (henceforth "PEB") is desirable. Although the heating condition changes according to the combination presentation of a radiation-curing nature constituent, the class of additive, etc., it is usually 50–150 degrees C preferably 30–200 degrees C.

[0043] Thus, pattern exposure can be carried out according to a predetermined pattern, and a development can be carried out to the thin film stiffened alternatively using the soluble

difference for a part for a hard spot, and a non-hard spot. Therefore, after pattern exposure, while removing a part for a non-hard spot, a core part can be formed as a result by making the amount of hard spot remain.

[0044] As a developer here An organic solvent or a sodium hydroxide, a potassium hydroxide, A sodium carbonate, a sodium silicate, a meta-sodium silicate, ammonia, Ethylamine, n propylamine, diethylamine, G n propylamine, Triethylamine, methyl diethylamine, N-methyl pyrrolidone, Dimethylethanolamine, triethanolamine, tetramethylammonium hydroxide, The alkali water solution which consists of alkali, such as a tetraethylammonium hydroxide, choline, pyrrole, piperidine, 1, 8-diazabicyclo [5.4.0]-7-undecene, 1, and 5-diazabicyclo [4.3.0]-5-nonane, can be used. Moreover, when using alkali water solubility, it is desirable to usually make the concentration into the value of 0.1 – 3.0% of the weight of within the limits preferably 0.05 to 25% of the weight. In addition, it is also desirable to carry out suitable amount addition of water-soluble organic solvents, surfactants, etc., such as a methanol and ethanol, and to use it for such an alkali water solution as a developer.

[0045] Moreover, developing time is usually for 30 – 600 seconds, and the development approach can adopt well-known approaches, such as a liquid peak method, a dipping method, and the shower developing-negatives method. being air-dry as it is, when an organic solvent is used as a developer — moreover — the case where an alkali water solution is used — a stream — washing — for example, a pattern-like coat is formed by carrying out for 30 – 90 seconds and removing the moisture on a front face by carrying out an air dried with the compressed air, compression nitrogen, etc. Subsequently, in order to stiffen the patterning section further, by heating apparatus, such as a hot plate and oven, postbake processing will be carried out for 5 – 600 minutes at the temperature of 30–400 degrees C, and the hardened core part will be formed.

[0046] ** **** of an up cladding layer — subsequently, apply the constituent for the upper layers to the front face of the lower cladding layer 13 in which the core part 15 was formed, make it dry or prebake, and form the thin film for the upper layers in it. By irradiating a radiation and besides, stiffening it to the thin film for layers, as shown in drawing 1, the up cladding layer 17 can be formed. Moreover, the up cladding layer obtained by the exposure of a radiation has the desirable thing which were further mentioned above if needed and to do for postbake. By carrying out postbake, the up cladding layer excellent in a degree of hardness and thermal resistance can be obtained.

[0047]

[Example] Hereafter, although an example explains this invention concretely, this invention is not limited to these examples.

[0048] [Preparation of a radiation-curing nature constituent]

After carrying out the nitrogen purge of the flask to which the example of preparation 1 dry ice / methanol dephlegmator of the copolymer for core parts (A) were attached, ethyl lactate was taught for 2 and 2'-azobisisobutyronitril as a polymerization initiator, and 53.8g was taught as 1.3g and an organic solvent, and it stirred until the polymerization initiator dissolved. Then, after teaching 6.7g [of methacrylic acids], and dicyclopentanil methacrylate 15.7g, styrene 9.0g, and n-butyl acrylate 13.5g, stirring was begun gently. Then, the temperature of a solution was raised at 80 degrees C, and the polymerization was performed at this temperature for 4 hours. Then, the resultant was dropped at a lot of hexanes, and the resultant was made to solidify.

Furthermore, it remelted to the tetrahydrofuran of this congelation and this weight, and was made to solidify again by a lot of hexanes. After performing this remelting-coagulation actuation a total of 3 times, the vacuum drying of the obtained congelation was carried out at 40 degrees C for 48 hours, and the target copolymer A-1 was obtained.

[0049] Example 2 of preparation of the copolymer for cladding layers (A) After carrying out the nitrogen purge of the flask to which dry ice / methanol dephlegmator was attached, ethyl lactate was taught for 2 and 2'-azobis dimethylvaleronitrile as a polymerization initiator, and 54.3g was taught as 0.5g and an organic solvent, and it stirred until the polymerization initiator dissolved. Then, after teaching 4.5g [of methacrylic acids], and dicyclopentanil methacrylate 9.0g, methyl methacrylate 20.4g, and n-butyl acrylate 11.3g, stirring was begun gently. Then, the temperature

of a solution was raised at 80 degrees C, and the polymerization was performed at this temperature for 4 hours. Then, the resultant was dropped at a lot of hexanes, and the resultant was made to solidify. Furthermore, it remelted to the tetrahydrofuran of this congelation and this weight, and was made to solidify again by a lot of hexanes. After performing this remelting-coagulation actuation a total of 3 times, the vacuum drying of the obtained congelation was carried out at 40 degrees C for 48 hours, and the target copolymer A-2 was obtained.

[0050] After carrying out the nitrogen purge of the flask to which the example of preparation 3 dry ice / methanol dephlegmator of the copolymer for core parts (A) were attached, ethyl lactate was taught for 2 and 2'-azobisisobutyronitril as a polymerization initiator, and 53.8g was taught as 1.3g and an organic solvent, and it stirred until the polymerization initiator dissolved. Then, after teaching 6.7g [of methacrylic acids], and isobornyl methacrylate 15.7g, styrene 9.0g, and n-butyl acrylate 13.5g, stirring was begun gently. Then, the temperature of a solution was raised at 80 degrees C, and the polymerization was performed at this temperature for 4 hours. Then, the resultant was dropped at a lot of hexanes, and the resultant was made to solidify.

Furthermore, it remelted to the tetrahydrofuran of this congelation and this weight, and was made to solidify again by a lot of hexanes. After performing this remelting-coagulation actuation a total of 3 times, the vacuum drying of the obtained congelation was carried out at 40 degrees C for 48 hours, and the target copolymer A-3 was obtained.

[0051] After carrying out the nitrogen purge of the flask to which the example of preparation 4 (example of comparison) dry ice / methanol dephlegmator of the copolymer for core parts (A) were attached, ethyl lactate was taught for 2 and 2'-azobisisobutyronitril as a polymerization initiator, and 53.8g was taught as 1.3g and an organic solvent, and it stirred until the polymerization initiator dissolved. Then, after teaching dicyclopentanil methacrylate 17.9g, styrene 9.1g, and n-butyl acrylate 17.9g, stirring was begun gently. Then, the temperature of a solution was raised at 80 degrees C, and the polymerization was performed at this temperature for 4 hours. Then, the resultant was dropped at a lot of hexanes, and the resultant was made to solidify. Furthermore, it remelted to the tetrahydrofuran of this congelation and this weight, and was made to solidify again by a lot of hexanes. After performing this remelting-coagulation actuation a total of 3 times, the vacuum drying of the obtained congelation was carried out at 40 degrees C for 48 hours, and the target copolymer A-4 was obtained.

[0052] After carrying out the nitrogen purge of the flask to which the example of preparation 5 (example of comparison) dry ice / methanol dephlegmator of the copolymer for cladding layers (A) were attached, ethyl lactate was taught for 2 and 2'-azobis dimethylvaleronitrile as a polymerization initiator, and 54.3g was taught as 0.5g and an organic solvent, and it stirred until the polymerization initiator dissolved. Then, after teaching 4.5g [of methacrylic acids], and methyl methacrylate 24.9g, and n-butyl acrylate 15.8g, stirring was begun gently. Then, the temperature of a solution was raised at 80 degrees C, and the polymerization was performed at this temperature for 4 hours. Then, the resultant was dropped at a lot of hexanes, and the resultant was made to solidify. Furthermore, it remelted to the tetrahydrofuran of this congelation and this weight, and was made to solidify again by a lot of hexanes. After performing this remelting-coagulation actuation a total of 3 times, the vacuum drying of the obtained congelation was carried out at 40 degrees C for 48 hours, and the target copolymer A-5 was obtained.

[0053] Copolymer A-1 in which the radiation-curing nature constituent J-1 carried out preparation **** The radiation-curing nature constituent J-1 was obtained by carrying out 48.5 weight sections addition of the 3.0 weight sections and the ethyl lactate, and mixing to homogeneity Irgcure.369 (made in Tiba Speciality Chemicals) which are the 6.5 weight sections and a radiation radical polymerization initiator about the 10.0 weight sections and trimethylolpropane triacrylate in the polyester polyfunctional acrylate (the Toagosei make, M8100) which is a polymerization reactivity constituent to the 32.0 weight sections.

[0054] Copolymer A-2 in which the radiation-curing nature constituent J-2 carried out preparation **** The radiation-curing nature constituent J-2 was obtained by carrying out 41.6 weight sections addition of the 3.0 weight sections and the ethyl lactate, and mixing to homogeneity Irgcure.369 (made in Tiba Speciality Chemicals) which are the 11.1 weight sections

and a radiation radical polymerization initiator about the 16.6 weight sections and trimethylolpropane triacrylate in the polyester polyfunctional acrylate (the Toagosei make, M8100) which is a polymerization reactivity constituent to the 27.7 weight sections.

[0055] Copolymer A-3 in which the radiation-curing nature constituent J-3 carried out preparation **** The radiation-curing nature constituent J-3 was obtained by carrying out 48.5 weight sections addition of the 3.0 weight sections and the ethyl lactate, and mixing to homogeneity Irgcure.819 (made in Tiba Speciality Chemicals) which are the 13.5 weight sections and a radiation radical polymerization initiator about the pentaerythritol thoria chestnut rate which is a polymerization reactivity constituent to the 35.0 weight sections.

[0056] Copolymer A-1 in which the radiation-curing nature constituent J-4 carried out preparation **** The radiation-curing nature constituent J-4 was obtained by carrying out 48.5 weight sections addition of the 3.0 weight sections and the ethyl lactate, and mixing to homogeneity SP170 (product made from the Asahi electrification) who are the 16.5 weight sections and a radiation cationic initiator about the polyfunctional oxirane compound (the Daicel Chemical Industries make, EPOLEAD GT 301) which is a polymerization reactivity constituent to the 32.0 weight sections.

[0057] Copolymer A-1 in which the radiation-curing nature constituent J-5 carried out preparation **** The radiation-curing nature constituent J-5 was obtained by carrying out 48.5 weight sections addition of the 3.0 weight sections and the ethyl lactate, and mixing to homogeneity Irgcure.369 (made in Tiba Speciality Chemicals) which are the 13.5 weight sections and a radiation radical polymerization initiator about the dipentaerythritol hexaacrylate (the Nippon Kayaku make, DPFA) which is a polymerization reactivity constituent to the 35.0 weight sections.

[0058] Copolymer A-4 in which the radiation-curing nature constituent J-6 carried out preparation (example of comparison) **** The radiation-curing nature constituent J-6 was obtained by carrying out 48.5 weight sections addition of the 3.0 weight sections and the ethyl lactate, and mixing to homogeneity Irgcure.369 (made in Tiba Speciality Chemicals) which are the 6.5 weight sections and a radiation radical polymerization initiator about the 10.0 weight sections and trimethylolpropane triacrylate in the polyester polyfunctional acrylate (the Toagosei make, M8100) which is a polymerization reactivity constituent to the 32.0 weight sections.

[0059] Copolymer A-5 in which the radiation-curing nature constituent J-7 carried out preparation (example of comparison) **** The radiation-curing nature constituent J-7 was obtained by carrying out 41.6 weight sections addition of the 3.0 weight sections and the ethyl lactate, and mixing to homogeneity Irgcure.369 (made in Tiba Speciality Chemicals) which are the 11.1 weight sections and a radiation radical polymerization initiator about the 16.6 weight sections and trimethylolpropane triacrylate in the polyester polyfunctional acrylate (the Toagosei make, M8100) which is a polymerization reactivity constituent to the 27.7 weight sections.

[0060] [Example 1]

(1) The formation radiation-curing nature constituent J-2 of the formation ** lower cladding layer of optical waveguide was applied by the spin coater on the front face of a silicon substrate, and was prebaked the condition for 120 degrees C and 10 minutes using the hot plate. Subsequently, the paint film which consists of a radiation-curing nature constituent J-2 was irradiated for 30 seconds, and radiation curing of the ultraviolet rays of the wavelength of 365nm and illuminance 20 mW/cm² was carried out to it. And this hardening film was made into the lower cladding layer with a thickness of 50 micrometers by carrying out postbake on 200 degrees C and the conditions of 1 hour.

[0061] ** The paint film was formed by the spin coater on the lower cladding layer, and prebake of formation of a core part, next the radiation-curing nature constituent J-1 was carried out on 120 degrees C and the conditions for 10 minutes using the hot plate. Then, through the photo mask which has a Rhine-like pattern with a width of face of 50 micrometers, the ultraviolet rays of 2 were irradiated for 30 seconds the wavelength of 365nm, and the illuminance of 20mW/cm², and radiation curing of the paint film was carried out to the paint film with a thickness of 50 micrometers it is thin from the radiation-curing nature constituent J-1. Next, PEB was performed for the paint film which carried out radiation irradiation the condition for 100 degrees .

C and 1 minute. Subsequently, it was immersed into the developer which consists of a tetramethylammonium hydroxide water solution (TMAH) the substrate which has the paint film which carried out radiation hardening 1.8%, and the unexposed part of a paint film was dissolved. Then, postbake was performed on 200 degrees C and the conditions of 1 hour, and the core part which has a Rhine-like pattern with a width of face of 10 micrometers was formed.

[0062] ** **** of an up cladding layer — subsequently the radiation-curing nature constituent J-2 was applied to the top face of the lower cladding layer which has a core part by the spin coater, and it prebaked on 120 degrees C and the conditions for 10 minutes using the hot plate. Then, the up cladding layer with a thickness of 50 micrometers was formed in the paint film which consists of a radiation-curing nature constituent J-2 by irradiating the ultraviolet rays of the wavelength of 365nm, and illuminance 20 mW/cm² for 30 seconds. Then, postbake of this up cladding layer was carried out on 200 degrees C and the conditions of 6 hours.

[0063] Optical waveguide was formed by the same technique as the above mentioned technique except [all] using the constituent shown in Table 2 instead of using the constituent which described examples 2-4, the [examples 1-3 of comparison] lower cladding layer, the core part, and the up cladding layer in the example 1.

[0064] (2) The case where core height and core width of face became "O", more than it, and the following configurations about the case where the configuration of 50**5 micrometers is formed, about the core configuration (height [of 50 micrometers] x Rhine width of face of 50 micrometers) designed by technique to have carried out the precision above of the optical waveguide configuration was made into "x." A result is shown in Table 2.

[0065] (3) transmission loss evaluation of optical waveguide — incidence of the light with a wavelength of 824nm was carried out from the end about the optical waveguide which consists of the lower cladding layer, core part, and up cladding layer which were obtained by doing in this way. And the waveguide loss per unit length was searched for by the cutting-back method by measuring the quantity of light which carries out outgoing radiation from the other end. A result is shown in Table 2.

[0066]

[Table 1]

		J-1	J-2	J-3	J-4	J-5	J-6	J-7	J-8
(A)	A-1	32.0	-	-	32.0	35.0	-	-	32.0
	A-2	-	27.7	-	-	-	-	-	-
	A-3	-	-	35.0	-	-	-	-	-
(B)	M8100	10.0	16.6	-	-	-	10.0	16.6	-
	トリメチローブラボンソリウムアクリレート	6.5	11.1	-	-	-	6.5	11.1	-
	ベンタエリスリトールトリアクリレート	-	-	13.5	-	-	-	-	-
	エポリードG T 301	-	-	-	16.5	-	-	-	-
(C)	Irgcure 369	3.0	3.0	-	-	3.0	3.0	3.0	3.0
	Irgcure 819	-	-	3.0	-	-	-	-	-
	SP170	-	-	-	3.0	-	-	-	-
	乳酸エチル	48.5	41.6	48.5	48.5	48.5	48.5	41.6	48.5
その他	A-4	-	-	-	-	-	32.0	-	-
	A-5	-	-	-	-	-	-	27.7	-
	イソブチニトリルアクリレート	-	-	-	-	-	-	-	16.5
合 計		100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

[0067]

[Table 2]

	実 施 例					比 較 例	
	1	2	3	4	5	1	2
光導波路構成							
下層クラッド層	J-2	J-2	J-2	J-2	J-7	J-7	J-7
コア部分	J-1	J-3	J-4	J-5	J-1	J-6	J-8
上層クラッド層	J-2	J-2	J-2	J-2	J-7	J-7	J-7
824 nmにおける コア・クラッド間の屈折率差 (Δn (%))	1.1	1.1	1.1	1.1	1.1	1.1	1.1
光導波路特性							
コア形状の精度	○	○	○	○	○	×	×
伝送損失[dB/cm]	0.3	0.3	0.4	0.3	0.4	>1.0	>1.0

[0068]

[Effect of the Invention] Optical waveguide can be fabricated now by using the radiation-curing nature constituent of this invention to a short time and high degree of accuracy very easily. Moreover, transmission loss with the low optical waveguide formed with the radiation-curing nature constituent of this invention was able to be acquired. Thus, according to the manufacture approach of the optical waveguide of this invention, optical waveguide can be efficiently manufactured now.

[Translation done.]

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TECHNICAL FIELD

[Field of the Invention] This invention relates to the manufacture approach of the optical waveguide and optical waveguide which are formed using the radiation-curing nature constituent for optical waveguide formation which can form the optical waveguide which is excellent in the waveguide configuration where the purpose configuration was balanced, or a transmission characteristic, and it.

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PRIOR ART

[Description of the Prior Art] Multimedia age is greeted and optical waveguide attracts attention as a transmission medium of light from the demand of large-capacity-izing of the information processing in an optical transmission system or a computer, and improvement in the speed. As such optical waveguide, quartz system waveguide is typical and, generally is manufactured according to the following processes.

** Form the lower cladding layer which consists of glass membrane by technique, such as the flame depositing method (FHD) and a CVD method, on a silicon substrate.

** Form the thin film of the minerals with which this differs from a refractive index on a lower cladding layer, and form a core part by carrying out patterning of this thin film using a reactive-ion-etching method (RIE).

** Form an up cladding layer by the flame depositing method further.

However, by such manufacture approach of quartz system waveguide, while the special manufacturing installation was required, problems, like production time starts for a long time were seen.

[0003] Then, by both developing an unexposed part as if the light of the specified quantity being irradiated and radiation curing of the predetermined location being carried out to the constituent containing the component in which radiation polymerization is possible, the artificers of this invention formed the core part etc. and have proposed the approach of manufacturing the optical waveguide which is excellent in a transmission characteristic. According to the manufacture approach of optical waveguide using such a radiation-curing nature constituent, the advantage that a short time can be manufactured only by developing negatives as compared with the manufacture approach of the conventional quartz system waveguide after irradiating the light of the specified quantity, and optical waveguide can be manufactured by low cost can be acquired. However, the case where it could be difficult to form the optical waveguide which has detailed width of face, or it could not form the optical waveguide which has the outstanding transmission characteristic even if it performs the manufacture approach of the above-mentioned optical waveguide using the radiation-curing nature constituent reported to the former was seen.

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EFFECT OF THE INVENTION

[Effect of the Invention] Optical waveguide can be fabricated now by using the radiation-curing nature constituent of this invention to a short time and high degree of accuracy very easily. Moreover, transmission loss with the low optical waveguide formed with the radiation-curing nature constituent of this invention was able to be acquired. Thus, according to the manufacture approach of the optical waveguide of this invention, optical waveguide can be efficiently manufactured now.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] This invention is made against the background of the above situations, and aims at offering the approach that the outstanding waveguide configuration, the optical waveguide which has the outstanding transmission characteristic, and such optical waveguide can be manufactured efficiently.

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MEANS

[Means for Solving the Problem] The structural unit to which this invention originates in the radical polymerization nature compound which has the (A) and (a) carboxyl group, (b) The structural unit originating in the radical polymerization nature compound which has an annular alkyl group and does not have a carboxyl group, And the copolymer which has a structural unit originating in (c) above (a) and radical polymerization nature compounds other than (b) ("Copolymer (A)" is said hereafter), the compound which has two or more polymerization sexual response radicals in the (B) molecule, And the radiation-curing nature constituent for optical waveguide formation characterized by containing (C) radiation polymerization initiator The optical waveguide which formed at least one of (it may be hereafter called a "radiation-curing nature constituent"), a cladding layer, and the core parts with this constituent, and its manufacture approach are offered.

[0006]

[Embodiment of the Invention] The radiation hardenability product copolymer for optical waveguide formation (A) can be obtained by carrying out radical copolymerization of the radical polymerization nature compound which has the radical polymerization nature compound and (b) annular alkyl group which have the (a) carboxyl group, and does not have a carboxyl group, (c) above (a), and the radical polymerization nature compounds other than (b) in a solvent.

[0007] As a radical polymerization nature compound (a) which has said carboxyl group, the methacrylic-acid derivative which has a carboxyl group and ester bonds, such as dicarboxylic acid;2-SAKUSHINO roil ethyl (meta) acrylate, such as monocarboxylic acid; maleic acids, such as an acrylic acid, a methacrylic acid, and a crotonic acid, a fumaric acid, a citraconic acid, mesaconic acid, and an itaconic acid, 2-MAREINO roil ethyl (meta) acrylate, and 2-hexahydro phthloyl ethyl (meta) acrylate, for example can be used. These compounds can be used combining independence or two sorts or more. In these, an acrylic acid, a methacrylic acid, and 2-hexahydro phthloyl ethyl (meta) acrylate are an acrylic acid and a methacrylic acid desirable still more preferably.

[0008] The rate of the structural unit originating in the radical polymerization nature compound which has the carbonyl group occupied in a copolymer (A) is 5 – 50 % of the weight, and is 10 – 40 % of the weight preferably. When it is hard coming to dissolve when this constituent is stiffened by optical exposure as the rate of this structural unit is less than 5 % of the weight, and an alkali development is performed, and it uses as a core part of optical waveguide, the core configuration as a design is not acquired and sufficient transmission characteristic is not acquired. Conversely, even if it exceeds 50 % of the weight, the thing of the configuration as a design is not obtained.

[0009] As a radical polymerization nature compound (b) which has said annular alkyl group and does not have a carbonyl group, cyclohexyl (meta) acrylate, 2-methylcyclohexyl (meta) acrylate, dicyclopentanil oxy-ethyl (meta) acrylate, isobornyl (meta) acrylate, dicyclopentanil(metha) acrylate, etc. can be mentioned, for example. These compounds can be used combining independence or two sorts or more. In these, dicyclopentanil(metha)acrylate is desirable.

[0010] The rate of the structural unit originating in the radical polymerization nature compound which has the annular alkyl group occupied in a copolymer (A), and does not have a carbonyl

group is 15 – 60 % of the weight, and is 20 – 50 % of the weight preferably. The molecular weight of the copolymer obtained as this rate is less than 15 % of the weight does not fully go up, but the hardening film of this constituent of 20-micrometer or more thickness becomes difficult, and the waveguide configuration of hope cannot be produced. Conversely, if it exceeds 60 % of the weight, the solubility over the solvent of the copolymer obtained falls, and in case a copolymer is prepared, a problem will arise.

[0011] said — others — a radical polymerization nature compound (c) is used in order to mainly control the mechanical property and refractive index of a copolymer (A) moderately. As such other radical polymerization nature compounds (c), acrylic-acid (meta) alkyl ester, acrylic-acid (meta) aryl ester, dicarboxylic acid diester, aromatic series vinyl, conjugation diolefins, a nitrile group content polymerization nature compound, a chlorine content polymerization nature compound, an amide joint content polymerization nature compound, and fatty-acid vinyl can be mentioned preferably. Specifically Methyl (meta) acrylate, ethyl (meta) acrylate, Isopropyl (meta) acrylate, n-butyl (meta) acrylate, Acrylic-acid (meta) alkyl ester, such as sec-butyl (meta) acrylate and t-butyl (meta) acrylate; Phenyl (meta) acrylate, Acrylic-acid (meta) aryl ester, such as benzyl (meta) acrylate; A diethyl maleate, Dicarboxylic acid diester, such as diethyl fumarate and itaconic-acid diethyl; Styrene, Alpha methyl styrene, m-methyl styrene, p-methyl styrene, vinyltoluene, Aromatic series vinyl, such as p-methoxy styrene; 1,3-butadiene, Conjugation diolefins, such as isoprene, 1, and 4-dimethylbutadiene Nitrile group content polymerization nature compounds, such as acrylonitrile and a methacrylonitrile; A vinyl chloride, Chlorine content polymerization nature compounds, such as a vinylidene chloride; fatty-acid vinyl [, such as amide joint content polymerization nature compound; vinyl acetate,], such as acrylamide and methacrylamide, can be used. These compounds can be used combining independence or two sorts or more, and methyl (meta) acrylate, n-butyl (meta) acrylate, styrene, especially its alpha methyl styrene, etc. are [among these] desirable. The rate of the structural unit originating in radical polymerization nature compounds other than (a) occupied in a copolymer (A) and (b) is 5 – 80 % of the weight, and is 20 – 70 % of the weight preferably.

[0012] As a polymerization solvent used in case a copolymer (A) is compounded For example, a methanol, ethanol, ethylene glycol, a diethylene glycol, Alcohols, such as propylene glycol; Cyclic ether; ethylene glycol monomethyl ether, such as a tetrahydrofuran and dioxane, Ethylene glycol monoethyl ether, ethylene glycol wood ether, Ethylene glycol diethylether, the diethylene-glycol monomethyl ether, Diethylene glycol monoethyl ether, diethylene-glycol wood ether, Diethylene-glycol diethylether, diethylene-glycol ethyl methyl ether, The alkyl ether of polyhydric alcohol, such as propylene glycol monomethyl ether and the propylene glycol monoethyl ether; Ethylene glycol ethyl ether acetate, The alkyl ether acetate of polyhydric alcohol, such as diethylene-glycol ethyl ether acetate and propylene glycol ethyl ether acetate; Toluene, Aromatic hydrocarbon, such as a xylene; An acetone, a methyl ethyl ketone, Methyl isobutyl ketone, a cyclohexanone, 4-hydroxy-4-methyl-2-pentanone, Ketones, such as diacetone alcohol; Ethyl acetate, butyl acetate, ethyl lactate, 2-hydroxy ethyl propionate, 2-hydroxy-2-methyl ethyl propionate, 2-hydroxy-2-methyl ethyl propionate, ethoxy ethyl acetate, Ester, such as hydroxyacetic acid ethyl, 2-hydroxy-3-methyl butanoic acid methyl, 3-methoxy methyl propionate, 3-methoxy ethyl propionate, 3-ethoxy ethyl propionate, and 3-ethoxy methyl propionate, is mentioned. Cyclic ether, the alkyl ether of polyhydric alcohol, the alkyl ether acetate of polyhydric alcohol, ketones, and ester are [among these] desirable.

[0013] Moreover, as a polymerization catalyst in radical copolymerization, the usual radical polymerization initiator can be used, for example, organic peroxide, such as an azo compound; benzoyl peroxide [, such as – azobis – (4-methoxy-2'-dimethylvaleronitrile)], lauroyl peroxide, t-butylperoxy pivalate, and 2 and 2(- azobisisobutyronitril, and '2, 2')-azobis – (2,4-dimethylvaleronitrile), 2, and 2 '1, 1'-screw-(t-butylperoxy) cyclohexane, a hydrogen peroxide, etc. can be mentioned. When using a peroxide for a radical polymerization initiator, it is good also as an initiator of a redox type combining a reducing agent. The desirable average molecular weight of the copolymer (A) obtained is 3,000–100,000. This molecular weight is defined by the polystyrene conversion called for by the gel permission chromatography (GPC). It becomes difficult to carry out coating of this constituent to molecular weight being less than 3,000 by

predetermined thickness on a substrate. On the contrary, if molecular weight exceeds 100,000, in case optical waveguide will be formed with this constituent, the target waveguide configuration may not be acquired.

[0014] The compounds (B) which have two or more polymerization sexual response radicals in the molecule which constitutes the constituent of this invention are thermal polymerization and/or a compound to photopolymerize, and can illustrate a compound as shown below.

The compound which has two or more ethylene nature partial saturation radicals in a molecule; (meta) the compound which contains an acryloyl radical or a vinyl group in [two or more] a molecule can be used. As such a compound, for example Ethylene GURIKORUJI (meta) acrylate, Tetra-ethylene GURIKORUJI (meta) acrylate, polyethylene GURIKORUJI (meta) acrylate, To 1, 4-butane JIORUJI (meta) acrylate, 1, and 6-, KISANJIORUJI (meta) acrylate, Neopentyl GURIKORUJI (meta) acrylate, tris (2-hydroxyethyl) iso SHIANURETOJI (meta) acrylate, Bis (hydroxymethyl) tricyclo DEKANJI (meta) acrylate, The di(meth)acrylate of the diol which is the adduct of the ethyleneoxide of bisphenol A, or propylene oxide, The di(meth)acrylate of the diol which is the adduct of the ethyleneoxide of hydrogenation bisphenol A, or propylene oxide, The epoxy (meta) acrylate which made acrylate (meta) add to the diglycidyl ether of bisphenol A, the diacrylate of polyoxyalkylene-ized bisphenol A, etc. are mentioned. As acrylate (meta) which furthermore contains three or more acryloyl (meta) radicals in a molecule The compound in which the acrylic acid (meta) three mols or more carried out the ester bond to the polyhydric alcohol which has three or more hydroxyl groups, For example, TORIMECHI roll pro pantry (meta) acrylate, pen TAERISURITORUTORI (meta) acrylate, Trimethylol propane TORIOKISHI ethyl (meta) acrylate, tris (2-hydroxy ethyl) iso SHIANURETOTORI (meta) acrylate, dipentaerythritol hexa (meta) acrylate, etc. are mentioned. Moreover, a polyether, polyester, the polyether acrylic oligomer that has a polyurethane frame, polyester acrylic oligomer, polyurethane acrylic oligomer, or poly epoxy acrylic oligomer can also be used for a principal chain.

[0015] as these commercial items — YUPIMA [] UV — SA1002 and SA2007 (above) The Mitsubishi Chemical make, screw coat #195, #230, #215, #260, #295, #300, #335H.P., # 360, #400, #540, and # — 700 and 3 — PA and GPT (above) The OSAKA ORGANIC CHEMICAL INDUSTRY make, light acrylate 4 EG-A, 9 EG-A, NP-A, DCP-A, BP-4EA, BP-4PA, PE-3A, PE-4A, DPE-6A (above, product made from the Kyoeisha chemistry), KAYARAD MANDA, HX-220, HX-620, R-551, R-712, R-604, R-684, PET-30, GPO-303, TMPTA, DPHA, D-310, D-330, DPCA-20, -30, -60, -120 (above) The Nippon Kayaku make, ARONIKKUSU M208, M210, M215, M220, M240, M305, M309, M310, M315, M325, M400, M1200, M6100, M6200, M6250, M7100, M8030, M8060, M8100, M8530, and M8560 — M9050 (above, Toagosei make), RIPOKISHI VR-77, VR-60, VR-90 (above) The Showa High Polymer make, Ebecryl 81, 83, 600, 629, 645, 745, 754, 767, 701, 755, 705, 770, 800, 805, 810, 830, 450, 1830, and 1870 (above) The product made from die cel UCB, the beam sets 575, 551B, 502H, and 102 (above, product made from the Arakawa chemistry), etc. are mentioned.

[0016] The compound which has two or more cyclic ether in a molecule; the compound which has two or more cyclic ether can be used into a molecule among an oxirane compound, an oxetane compound, an oxo-run compound, etc. For example, it is 3 and 4-epoxycyclohexyl methyl as oxirane compounds. - 3', 4'-epoxy cyclohexane carboxylate, 2-(3, 4-epoxycyclohexyl - 5, 5-spiro -3, 4-epoxy) cyclohexane-metadioxane, A bis(3, 4-epoxycyclohexyl methyl) horse mackerel peat, a bis(3, 4-epoxy-6-methylcyclohexyl methyl) horse mackerel peat, 3, 4-epoxy-6-methylcyclohexyl - 3', 4' - epoxy -6'-methylcyclohexane carboxylate, Methylenabis (3, 4-epoxy cyclohexane), dicyclopentadiene diepoxide, The JI (3, 4-epoxycyclohexyl methyl) ether of ethylene glycol, An ethylene screw (3, 4-epoxy cyclohexane carboxylate), Epoxidation tetra-benzyl alcohol, the lactone denaturation 3, 4-epoxycyclohexyl methyl - 3', 4'-epoxy cyclohexane carboxylate, Lactone denaturation epoxidation tetrahydro benzyl alcohol, cyclohexene oxide, Bisphenol A diglycidyl ether, bisphenol F diglycidyl ether, Bisphenol S diglycidyl ether, hydrogenation bisphenol A diglycidyl ether, Hydrogenation bisphenol F diglycidyl ether, hydrogenation bisphenol A D diglycidyl ether, Bromination bisphenol A diglycidyl ether, bromination bisphenol F diglycidyl ether, Bromination bisphenol S diglycidyl ether, epoxy novolak resin, 1,4-butanediol diglycidyl ether, 1, 6-hexanediol diglycidyl ether, Glycerol triglycidyl ether,

trimethylolpropane triglycidyl ether, Polyethylene glycol diglycidyl ether and polypropylene glycol diglycidyl ether; Ethylene glycol, Propylene glycol, By adding one sort or two sorts or more of alkylene oxide to aliphatic series polyhydric alcohol, such as a glycerol The monoglycidyl ether of the diglycidyl ester; aliphatic series higher alcohol of the Pori glycidylethers; aliphatic series long-chain dibasic acid of the polyether polyol obtained; A phenol, The glycidyl ester of a monoglycidyl ether; higher fatty acid of the polyether alcohol which adds alkylene oxide to cresol, butylphenol, or these, and is obtained; Epoxidized soybean oil, Epoxy butyl stearate, epoxy stearin acid octyl, the epoxidation linseed oil, etc. can be mentioned. As an oxetane compound, 3, a 7-bis(3-OKISETANIRU)-5-OKISA-nonane, 3 and 3'-(1, 3-(2-MECHIRENIRU) propane diyl screw (oxy-methylene)) screw - (3-ethyl oxetane), 1, 4-bis[(3-ethyl-3-OKISETA nil methoxy) methyl] benzene, 1, 2-bis[(3-ethyl-3-OKISETA nil methoxy) methyl] ethane, 1, a 3-bis[(3-ethyl-3-OKISETA nil methoxy) methyl] propane, The ethylene glycol bis(3-ethyl-3-OKISETA nil methyl) ether, The JISHIKURO pentenyl bis(3-ethyl-3-OKISETA nil methyl) ether, The triethylene glycol bis(3-ethyl-3-OKISETA nil methyl) ether, The tetraethylene glycol bis(3-ethyl-3-OKISETA nil methyl) ether, The tricyclodecane diyl dimethylene (3-ethyl-3-OKISETA nil methyl) ether, The trimethylol propane tris (3-ethyl-3-OKISETA nil methyl) ether, 1, 4-bis(3-ethyl-3-OKISETA nil methoxy) butane, 1, a 6-bis(3-ethyl-3-OKISETA nil methoxy) hexane, The pentaerythritol tris (3-ethyl-3-OKISETA nil methyl) ether, The pentaerythritol tetrakis (3-ethyl-3-OKISETA nil methyl) ether etc. can be illustrated, and these can be used combining independent one sort or two sorts or more.

[0017] As these commercial items, the EPO lights 40E, 100E, and 70P, 1500NP, 100MF, 4000 and 3002 (above, product made from the Kyoeisha chemistry), the SEROKI sides 2021 and 2081, GT301 and GT401, EPOLEAD CDM, PB3600, the EPO friends A1005, A1010, and A1020 (above, Daicel Chemical Industries make), DENAKORU 611, 612, 512, 521, 411, 421, 313, and 321 (above, Nagase Brothers formation make), etc. are mentioned.

[0018] Moreover, you may be the compound which contains the above mentioned ethylene nature partial saturation radical and both at least one or more reactivity radicals of cyclic ether in a molecule, respectively. For example, glycidyl (meta) acrylate, vinyl cyclohexene oxide, 4-vinyl epoxy cyclohexane, 3, and 4-epoxycyclohexyl methyl (meta) acrylate etc. is mentioned. As for these compounds (B), it is desirable to use the compound which may use by independence or two sorts or more, and contains an ethylene nature partial saturation radical in [two or more] a molecule especially. the (Copolymer A) 100 weight section — receiving — desirable — the 30 — 150 weight section — it is the 50 — 130 weight section more preferably. In case optical waveguide is formed in case of under 30 weight sections, when the target waveguide configuration may not be acquired and the 150 weight sections are exceeded, compatibility with a copolymer (A) may worsen and may produce a film dry area on a hardened material front face.

[0019] The radiation polymerization initiator (C) which constitutes the constituent of this invention is an initiator which can generate the active species which can carry out the polymerization of the compound (B) described above with the radiation. A radiation means infrared radiation, a visible ray, ultraviolet rays and an X-ray, an electron ray, alpha rays, beta rays, and ionizing radiation like a gamma ray here. Therefore, the radiation polymerization initiator which is a component (C) is needed, and a photosensitizer is added further if needed. It can divide roughly into what decomposes by optical exposure and generates a radical as a radiation polymerization initiator (radiation radical polymerization initiator), and the thing (radiation cationic initiator) which generates a cation.

[0020] As a radiation radical polymerization initiator, for example An acetophenone, acetophenone benzyl ketal, A 1-hydroxy cyclohexyl phenyl ketone, 2, and 2-dimethoxy-2-phenyl acetophenone, xanthone and full — me — non and ** NZUARUDEHIDO, a fluorene, and anthraquinone — A triphenylamine, a carbazole, 3-methylacetophenone, 4-chlorobenzophenone, A 4 and 4'-dimethoxy benzophenone, 4, and 4'-diamino benzophenone, A Michler's ketone, the benzoin propyl ether, benzoin ethyl ether, Benzyl dimethyl ketal, 1-(4-isopropyl phenyl)-2-hydroxy-isobutane-1-ON, 2-hydroxy-2-methyl-1-phenyl propane-1-ON, a thioxan ton, A diethyl thioxan ton, 2-isopropyl thioxan ton, 2-chloro thioxan ton, 2-methyl-1-[4-(methylthio) phenyl]-2-morpholino-propane-1-ON, 2, 4, 6-trimethyl benzoyl diphenyl phosphine oxide, and

screw-(2, 6-dimethoxybenzoyl)- 2, 4, and 4-trimethyl pentyl phosphoretted hydrogen oxide etc. is mentioned.

[0021] As a commercial item of a radiation radical polymerization initiator, Irgacure 184, 369, 651, 500, 819, 907, 784, and 2959, CGI1700, CGI1750, CGI11850 and CG 24-61, Darocurl 116 and 1173 (above, made in Tiba Speciality Chemicals), LucirinTPO, TPO-L (above, BASF make), YUBEKURIRU P36 (product made from UCB), etc. are mentioned, for example.

[0022] The onium salt which has the structure expressed with the following general formula (1) as a radiation cationic initiator can be mentioned. This onium salt is a compound which emits Lewis acid by receiving light.

[R12a R13b R14c R15d W]+m[MXn+m]-m (1)

It is that R12, R13, R14, and R15 are the same or a different organic radical, and a cation is onium ion among [type and (a+b+c+d) is [W is S, Se, Te, P As, Sb Bi, O, I, Br, Cl, or N**N, and / a, b, c, and d are the integers of 0-3, respectively, and] equal to the valence of W. M is the metal or metalloid which constitutes the neutral atom of a halogenide complex [MXn+m], for example, is B, P, As, Sb, Fe, Sn, Bi, aluminum, calcium, In, Ti, Zn, Sc, V, Cr, Mn, Co, etc. X is halogen atoms, such as F, Cl, and Br, m is the charge of the net of halogenide complex ion, and n is the valence of M.]

In a general formula (1) as an example of onium ion Diphenyliodonium, 4-methoxy diphenyliodonium, bis(4-methylphenyl) iodonium, Bis(4-tert-butylphenyl) iodonium, bis(dodecyl phenyl) iodonium, Triphenylsulfonium, diphenyl-4-thio phenoxyphenyl sulfonium, A bis[4-(diphenyl SURUFONIO)-phenyl] sulfide, a bis[4-(JI (4-(2-hydroxyethyl) phenyl) SURUHONIO)-phenyl] sulfide, eta5-2 and 4-(cyclo pen TAJIENIRU) [1, 2, 3, 4, 5, and 6-eta-(methylethyl)-benzene]-iron (1+) etc. is mentioned.

[0023] As an example of the anion (MXn+m) in the above-mentioned general formula (1), tetrafluoroborate (BF4-), hexafluorophosphate (PF6-), hexafluoroantimonate (SbF6-), hexafluoroarsenate (AsF6-), hexa chloro antimonate (SbCl6-), etc. are mentioned. As onium salt which can be used as a radiation cationic initiator, it sets to said general formula (27), and is general formula: [MXn(OH)-] instead of [MXn+m].

(— here, M, X, and n are as a definition about a general formula (1).) — the onium salt which has other anions, such as the anion expressed, perchloric acid ion (ClO4-), trifluoro methysulfonic acid ion (CF3SO3-), fluorosulfonic acid ion (FSO3-), toluenesulfonic acid ion, trinitrobenzene sulfonic acid ion, and trinitrotoluene sulfonic acid ion, is mentioned.

[0024] As a commercial item of a radiation cationic initiator For example, UVI-6950, UVI-6970, UVI-6974, UVI-6990 (above) Union Carbide, ADEKAOPUTOMA SP-150, SP-151, SP-170, SP-171 (above) Asahi Denka Kogyo K.K., Irgacure 261 (above, Ciba-Geigy), CI-2481, CI-2624, CI-2639, CI-2064 (above) Nippon Soda Co., Ltd., CD-1010, CD-1011, CD-1012 (above) Sartomer, DTS-102, DTS-103, NAT-103, NDS-103, TPS-102, TPS-103, MDS-103, MPI-103, BBI-101, BBI-102, BBI-103 (above) Green Chemistry, Degacure K126 (Degussa AG make) etc. is mentioned. The aforementioned radiation polymerization initiator can constitute the (C) component combining one-sort independence or two or more sorts of things.

[0025] When it is made into a component (A) and the total quantity 100 weight section of (B), as for the content rate of the (C) component in the radiation-curing nature constituent of this invention, it is desirable that it is usually 0.1 – 20 weight section, and it is desirable that it is especially 0.2 – 10 weight section. (C) When the content rate of a component is under the 0.1 weight section, hardening may not fully advance but may produce a problem in the transmission characteristic of optical waveguide. On the other hand, if 20 weight sections are exceeded, an initiator may have a bad influence on a long-term transmission characteristic.

[0026] Moreover, in a radiation-curing nature constituent, it is also desirable to use together with the radiation polymerization initiator mentioned above, and to blend a photosensitizer. This reason is because energy lines, such as light, can be absorbed more effectively by using a photosensitizer together. as such a photosensitizer — derivative [of a thioxan ton, a diethyl thioxan ton, and a thioxan ton]; — a derivative; coumarin, a keto coumarin, etc. of the derivative; xanthone of the derivative; anthracene of anthraquinone, bromine anthraquinone, and anthraquinone, a bromine anthracene, anthracene derivative; perylene, and perylene, a thioxan

ton, and a thioxan ton can be mentioned. These photosensitizers need to choose the sensitizer for which it was suitable according to the class of initiator.

[0027] In the radiation-curing nature constituent of this invention, in the range which does not spoil the property of the radiation-curing nature constituent of this invention if needed other than the aforementioned component For example, the compound and macromolecule resin which contain one polymerization sexual response radical in a molecule, For example, an epoxy resin, acrylic resin, polyamide resin, polyamidoimide resin, Polyurethane resin, a polybutadiene resin, polychloroprene resin, polyether resin, Polyester resin, a styrene-butadiene block copolymer, petroleum resin, xylene resin, ketone resin, cellulosic resin, a fluorine system polymer, and a silicone system polymer polymer can be blended.

[0028] An antioxidant, an ultraviolet ray absorbent, light stabilizer, a silane coupling agent, a painted-surface amelioration agent, thermal polymerization inhibitor, a leveling agent, a surfactant, a coloring agent, a preservation stabilizer, a plasticizer, lubricant, a filler, a particle, an antioxidant, a wettability amelioration agent, an antistatic agent, etc. can be blended as various additives further again if needed in addition to the above-mentioned component. Here, as an antioxidant, it is Irganox 1010, 1035, 1076, and 1222 (above), for example. The product made from tiba SUPESHARUTI KEMIKARUZU, Antigene P, 3C, FR, Sumi Reiser (Sumitomo Chemical make), etc. are mentioned. As an ultraviolet ray absorbent For example, Tinuvin P, 234, 320, 326, 327, 328, 329, 213 (above) The product made from tiba SUPESHARUTI KEMIKARUZU, Seesorb 102, 103, 110, 501, 202, 712, and 704 (above, SHIPRO formation make), etc. are mentioned. As light stabilizer For example, Tinuvin 292, 144, 622LD (above, product made from tiba SUPESHARUTI KEMIKARUZU), SANORU [LS and Sumisorb] 770 (Sankyo make) TM-061 (Sumitomo Chemical make) etc. is mentioned. As a silane coupling agent for example, as gamma-aminopropyl triethoxysilane, gamma-mercaptopropyltrimethoxysilane, gamma-meta-acryloxypropyltrimethoxysilane, and a commercial item SH 6062 and 6030 (above, Dow Corning Toray Silicone make), KBE 903, 603, and 403 (above, Shin-Etsu Chemical make), etc. are mentioned. As a painted-surface amelioration agent For example, silicone additives, such as a dimethylsiloxane polyether, are mentioned. As a commercial item, DC-57, DC-190 (above, Dow Corning make), SH 1 28PA, SH-29PA, SH-30PA, SH-190 (above) The Dow Corning Toray Silicone make, KF351, KF352, KF353 and KF354 (above, Shin-Etsu Chemical make), L-700, L-7002, L-7500, FK-024-90 (above, Nippon Unicar make), etc. are mentioned.

[0029] As for the radiation-curing nature constituent of this invention, it is still more desirable as a (D) component to contain an organic solvent. Since suitable viscosity can be obtained while the preservation stability of a radiation-curing nature constituent improves by adding an organic solvent, the optical waveguide which has uniform thickness can be formed.

[0030] Although it can choose as a class of organic solvent in the range which does not spoil the purpose of this invention, and effectiveness, it is usually desirable that the boiling point under atmospheric pressure is the organic compound which has a value within the limits which are 50-200 degrees C, and it is the organic compound made to dissolve each constituent in homogeneity. The organic solvent specifically used in case the copolymer of a component (A) is prepared can be used. As a desirable organic solvent, alcohols, ester, and ketones are mentioned and at least one solvent chosen from the group which consists of propylene glycol monomethyl ether, ethyl lactate, methyl isobutyl ketone, methyl amyl ketone, toluene, a xylene, and a methanol is mentioned as a more desirable organic solvent.

[0031] When it is made into the AUW 100 weight section of (C) from a component (A), as for the content of an organic solvent, it is desirable to consider as the value of the 10 - 200 weight section within the limits. It is because the viscosity control of a radiation-curing nature constituent may become difficult if the addition of this organic solvent becomes under 10 weight sections, and is because it may become difficult to form the optical waveguide which has sufficient thickness if the addition of an organic solvent exceeds the 200 weight sections on the other hand.

[0032] The radiation-curing nature constituent of this invention chooses suitably the class of the above-mentioned (A) component and (B) component, loadings, etc., in order to consider as a refractive index required for the part to be used, i.e., a cladding layer, and a core part. In case

the radiation-curing nature constituent of this invention is prepared, it is desirable to make the viscosity into the value within the limits of 1-10,000cps (25 degrees C), it is more desirable to consider as the value within the limits of 5-8,000cps (25 degrees C), and it is still more desirable to consider as the value within the limits of 10-5,000cps (25 degrees C).

[0033] Optical waveguide drawing 1 is the sectional view showing the fundamental configuration of the optical waveguide constituted with the application of the radiation-curing nature constituent of this invention. As shown in this drawing 1, optical waveguide is constituted including the substrate 12 extended in the direction of a right angle (the depth direction) in space, the lower cladding layer 13 formed on the front face of this substrate 12, the core part 15 which was formed on this lower cladding layer 13 and which has specific width of face, and the up cladding layer 17 formed by carrying out a laminating on the lower cladding layer 13 containing this core part 15. And as waveguide loss decreases, the core part 15 is covered with the lower cladding layer 13 and the up cladding layer 17 including the flank, and is in the condition laid underground as a whole.

[0034] In the optical waveguide of the above configurations, although especially the thickness of a lower cladding layer, an up cladding layer, and a core part is not restricted, respectively, it is desirable to, make [lower clad layer thickness] 3-200 micrometers and up clad layer thickness into the value within the limits of 1-200 micrometers for the thickness of 1-200 micrometers and a core part for example. Moreover, although not limited especially about the width of face of a core part, either, it is desirable to consider as the value within the limits of 1-200 micrometers for example.

[0035] Moreover, it is required to make the refractive index of a core part larger than which refractive index of the lower part and an up cladding layer. Therefore, while making the refractive index of a core part into the value of 1.420-1.650 within the limits to light with a wavelength of 400-1,600nm, it is desirable to make the refractive index of a lower cladding layer and an up cladding layer into the value of 1.400-1.648 within the limits, respectively. Moreover, it is desirable that the refractive-index difference of a core part and a cladding layer is separated 0.1% or more, and it is desirable to make especially the refractive index of a core part into a value larger at least 0.1% than the refractive index of a cladding layer. As for the optical waveguide of this invention, at least one of the above-mentioned cladding layer and the core parts consists of a hardened material of the radiation-curing nature constituent of this invention. The cladding layer and core part which are not formed with the hardened material of the radiation-curing nature constituent of this invention can be formed by polyimide, polyacrylate, the polycarbonate, a polysiloxane, etc.

[0036] Optical waveguide is formed through a process as shown in drawing 2. That is, after carrying out coating of the radiation-curing nature constituent for forming those layers for each of lower cladding layers 13, core parts 15, and up cladding layers (not shown), it is desirable to form by carrying out radiation curing. In addition, the following examples of formation explain a lower cladding layer, a core part, and an up cladding layer supposing forming from the constituent for lower layers which is a radiation-curing nature constituent with which the hardened material with which refractive indexes differ after hardening, respectively is obtained, the constituent for cores, and the constituent for the upper layers. And it is desirable to use as the constituent for cores the radiation-curing nature constituent which gives the hardening film of the highest refractive index using two sorts or three sorts of radiation-curing nature constituents with which the difference of a refractive index serves as proper magnitude, and to use other radiation-curing nature constituents as the constituent for lower layers and a constituent for the upper layers. However, the constituent for lower layers and the constituent for the upper layers may be the same radiation-curing nature constituents, it is economically advantageous that it is the usually same constituent, and it is more desirable from manufacture management becoming easy.

[0037] ** As shown in preparation **** of a substrate, and drawing 2 (a), prepare the substrate 12 which has a flat front face. Especially as a class of this substrate 12, although not restricted, a silicon substrate, a glass substrate, etc. can be used, for example.

[0038] ** It is the process which forms the lower cladding layer 13 in the front face of the

substrate 12 in which the lower cladding layer carried out formation process preparation. As shown in drawing 2 (b), apply the constituent for lower layers to the front face of a substrate 12, it is made to dry or prebake, and, specifically, the thin film for lower layers is formed in it. And this thin film for lower layers can be stiffened by irradiating a radiation, and the lower cladding layer 13 can be formed. In addition, it is desirable to irradiate a radiation all over a thin film and to harden the whole in the formation process of the lower cladding layer 13.

[0039] Here, as the method of application, approaches, such as a spin coat method, a dipping method, a spray method, the bar coat method, the roll coat method, the curtain coat method, gravure, the silk screen method, or the ink jet method, can be used for the constituent for lower layers. Among these, since the thin film for lower layers of uniform thickness is obtained especially, it is more desirable to adopt a spin coat method. Moreover, since the rheology property of the constituent for lower layers should be appropriately corresponded to the method of application, it is desirable to blend various leveling agents, a CHIKUSO grant agent, a filler, an organic solvent, a surfactant, etc. if needed. Moreover, as for the thin film for lower layers which consists of a constituent for lower layers, it is desirable after spreading to prebake at the temperature of 50–200 degrees C in order to remove an organic solvent etc. In addition, they are the contents which are applied also in the formation process of the core part mentioned later, and the formation process of an up cladding layer about the method of application in the formation process of a lower cladding layer, and amelioration of a rheology property.

[0040] Moreover, although there is nothing also about the exposure of the radiation at the time of forming a lower cladding layer especially at the thing restricted, it is desirable to irradiate the radiation of 2 so that an exposure may serve as 10 – 5,000 mJ/cm², and to expose it the wavelength of 200–390nm and the illuminance of 0.1–500mW/cm. Although the light, ultraviolet rays, infrared radiation, an X-ray, alpha rays, beta rays, a gamma ray, etc. can be used here as a class of radiation irradiated, especially ultraviolet rays are desirable. And as irradiation equipment of a radiation (ultraviolet rays), it is desirable to, use a high-pressure mercury lamp, a low-pressure mercury lamp, a metal halide lamp, an excimer lamp, etc. for example. Moreover, heat-treating further (henceforth "postbake") is desirable so that the whole paint film surface may harden enough after exposure. What is necessary is to be 50–300 degrees C preferably, for example, just to usually make it into the heating conditions of for [5 minutes] – 72 hours 30–400 degrees C, although this heating condition changes according to the combination presentation of a radiation-curing nature constituent, the class of additive, etc. In addition, they are the contents which are applied also in the formation process of the core part mentioned later, and the formation process of an up cladding layer about the exposure of the radiation in the formation process of a lower cladding layer, a class, and the irradiation equipment of a radiation (ultraviolet rays).

[0041] ** it is shown on formation, next this lower cladding layer 13 of a core part at drawing 2 (c) — as — the constituent for cores — applying — desiccation — or make it prebake further and form the thin film 14 for cores. Then, as shown in drawing 2 (d), it is desirable to irradiate a radiation 16 to the top face of the thin film 14 for cores through the photo mask 19 which has the predetermined Rhine pattern according to a predetermined pattern. Since only the part where the radiation was irradiated hardens by this, as shown in drawing 2 (e), the core part 15 which consists of hardening film by which patterning was carried out can be formed on the lower cladding layer 13 by carrying out development removal of the part which is not hardened [other].

[0042] Moreover, after the exposure of the radiation 16 to the thin film 14 for cores for forming the core part 15 is performed according to the photo mask 19 which has a predetermined pattern, by developing a part for an unexposed part with a developer, an unnecessary non-hardened part is removed and the core part 15 is formed of this. Thus, the approach of a-c which it is not restricted to the approach using the photo mask which consists of the transparency section and the nontransparent section of a radiation as an approach of irradiating a radiation according to a predetermined pattern, for example, is shown below is mentioned.
a. How to use a means to form the mask image using the same principle as a liquid crystal display which consists of a radioparency field and a radiopacity field according to a

predetermined pattern in electro-optics.

b. How to irradiate a radiation through the optical fiber corresponding to the predetermined pattern in this light guide section material using the light guide section material which comes to bundle many optical fibers.

c. How to irradiate a radiation-curing nature constituent, while making the convergent radiation obtained according to condensing nature optical system, such as a laser beam or a lens, and a mirror, scan.

In addition, after exposure, in order to promote hardening of an exposure part, heat-treating (henceforth "PEB") is desirable. Although the heating condition changes according to the combination presentation of a radiation-curing nature constituent, the class of additive, etc., it is usually 50–150 degrees C preferably 30–200 degrees C.

[0043] Thus, pattern exposure can be carried out according to a predetermined pattern, and a development can be carried out to the thin film stiffened alternatively using the soluble difference for a part for a hard spot, and a non-hard spot. Therefore, after pattern exposure, while removing a part for a non-hard spot, a core part can be formed as a result by making the amount of hard spot remain.

[0044] As a developer here An organic solvent or a sodium hydroxide, a potassium hydroxide, A sodium carbonate, a sodium silicate, a meta-sodium silicate, ammonia, Ethylamine, n propylamine, diethylamine, G n propylamine, Triethylamine, methyl diethylamine, N-methyl pyrrolidone, Dimethylethanolamine, triethanolamine, tetramethylammonium hydroxide, The alkali water solution which consists of alkali, such as a tetraethylammonium hydroxide, choline, pyrrole, piperidine, 1, 8-diazabicyclo [5.4.0]-7-undecene, 1, and 5-diazabicyclo [4.3.0]-5-nonane, can be used. Moreover, when using alkali water solubility, it is desirable to usually make the concentration into the value of 0.1 – 3.0% of the weight of within the limits preferably 0.05 to 25% of the weight. In addition, it is also desirable to carry out suitable amount addition of water-soluble organic solvents, surfactants, etc., such as a methanol and ethanol, and to use it for such an alkali water solution as a developer.

[0045] Moreover, developing time is usually for 30 – 600 seconds, and the development approach can adopt well-known approaches, such as a liquid peak method, a dipping method, and the shower developing–negatives method. being air-dry as it is, when an organic solvent is used as a developer — moreover — the case where an alkali water solution is used — a stream — washing — for example, a pattern-like coat is formed by carrying out for 30 – 90 seconds and removing the moisture on a front face by carrying out an air dried with the compressed air, compression nitrogen, etc. Subsequently, in order to stiffen the patterning section further, by heating apparatus, such as a hot plate and oven, postbake processing will be carried out for 5 – 600 minutes at the temperature of 30–400 degrees C, and the hardened core part will be formed.

[0046] ** **** of an up cladding layer — subsequently, apply the constituent for the upper layers to the front face of the lower cladding layer 13 in which the core part 15 was formed, make it dry or prebake, and form the thin film for the upper layers in it. By irradiating a radiation and besides, stiffening it to the thin film for layers, as shown in drawing 1, the up cladding layer 17 can be formed. Moreover, the up cladding layer obtained by the exposure of a radiation has the desirable thing which were further mentioned above if needed and to do for postbake. By carrying out postbake, the up cladding layer excellent in a degree of hardness and thermal resistance can be obtained.

[Translation done.]

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- 2.**** shows the word which can not be translated.
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EXAMPLE

[Example] Hereafter, although an example explains this invention concretely, this invention is not limited to these examples.

[0048] [Preparation of a radiation-curing nature constituent]

After carrying out the nitrogen purge of the flask to which the example of preparation 1 dry ice / methanol dephlegmator of the copolymer for core parts (A) were attached, ethyl lactate was taught for 2 and 2'-azobisisobutyronitril as a polymerization initiator, and 53.8g was taught as 1.3g and an organic solvent, and it stirred until the polymerization initiator dissolved. Then, after teaching 6.7g [of methacrylic acids], and dicyclopentanil methacrylate 15.7g, styrene 9.0g, and n-butyl acrylate 13.5g, stirring was begun gently. Then, the temperature of a solution was raised at 80 degrees C, and the polymerization was performed at this temperature for 4 hours. Then, the resultant was dropped at a lot of hexanes, and the resultant was made to solidify.

Furthermore, it remelted to the tetrahydrofuran of this congelation and this weight, and was made to solidify again by a lot of hexanes. After performing this remelting-coagulation actuation a total of 3 times, the vacuum drying of the obtained congelation was carried out at 40 degrees C for 48 hours, and the target copolymer A-1 was obtained.

[0049] Example 2 of preparation of the copolymer for cladding layers (A) After carrying out the nitrogen purge of the flask to which dry ice / methanol dephlegmator was attached, ethyl lactate was taught for 2 and 2'-azobis dimethylvaleronitrile as a polymerization initiator, and 54.3g was taught as 0.5g and an organic solvent, and it stirred until the polymerization initiator dissolved. Then, after teaching 4.5g [of methacrylic acids], and dicyclopentanil methacrylate 9.0g, methyl methacrylate 20.4g, and n-butyl acrylate 11.3g, stirring was begun gently. Then, the temperature of a solution was raised at 80 degrees C, and the polymerization was performed at this temperature for 4 hours. Then, the resultant was dropped at a lot of hexanes, and the resultant was made to solidify. Furthermore, it remelted to the tetrahydrofuran of this congelation and this weight, and was made to solidify again by a lot of hexanes. After performing this remelting-coagulation actuation a total of 3 times, the vacuum drying of the obtained congelation was carried out at 40 degrees C for 48 hours, and the target copolymer A-2 was obtained.

[0050] After carrying out the nitrogen purge of the flask to which the example of preparation 3 dry ice / methanol dephlegmator of the copolymer for core parts (A) were attached, ethyl lactate was taught for 2 and 2'-azobisisobutyronitril as a polymerization initiator, and 53.8g was taught as 1.3g and an organic solvent, and it stirred until the polymerization initiator dissolved. Then, after teaching 6.7g [of methacrylic acids], and isobornyl methacrylate 15.7g, styrene 9.0g, and n-butyl acrylate 13.5g, stirring was begun gently. Then, the temperature of a solution was raised at 80 degrees C, and the polymerization was performed at this temperature for 4 hours. Then, the resultant was dropped at a lot of hexanes, and the resultant was made to solidify.

Furthermore, it remelted to the tetrahydrofuran of this congelation and this weight, and was made to solidify again by a lot of hexanes. After performing this remelting-coagulation actuation a total of 3 times, the vacuum drying of the obtained congelation was carried out at 40 degrees C for 48 hours, and the target copolymer A-3 was obtained.

[0051] After carrying out the nitrogen purge of the flask to which the example of preparation 4 (example of comparison) dry ice / methanol dephlegmator of the copolymer for core parts (A)

were attached, ethyl lactate was taught for 2 and 2'-azobisisobutyronitril as a polymerization initiator, and 53.8g was taught as 1.3g and an organic solvent, and it stirred until the polymerization initiator dissolved. Then, after teaching dicyclopentanil methacrylate 17.9g, styrene 9.1g, and n-butyl acrylate 17.9g, stirring was begun gently. Then, the temperature of a solution was raised at 80 degrees C, and the polymerization was performed at this temperature for 4 hours. Then, the resultant was dropped at a lot of hexanes, and the resultant was made to solidify. Furthermore, it remelted to the tetrahydrofuran of this congelation and this weight, and was made to solidify again by a lot of hexanes. After performing this remelting-coagulation actuation a total of 3 times, the vacuum drying of the obtained congelation was carried out at 40 degrees C for 48 hours, and the target copolymer A-4 was obtained.

[0052] After carrying out the nitrogen purge of the flask to which the example of preparation 5 (example of comparison) dry ice / methanol dephlegmator of the copolymer for cladding layers (A) were attached, ethyl lactate was taught for 2 and 2'-azobis dimethylvaleronitrile as a polymerization initiator, and 54.3g was taught as 0.5g and an organic solvent, and it stirred until the polymerization initiator dissolved. Then, after teaching 4.5g [of methacrylic acids], and methyl methacrylate 24.9g, and n-butyl acrylate 15.8g, stirring was begun gently. Then, the temperature of a solution was raised at 80 degrees C, and the polymerization was performed at this temperature for 4 hours. Then, the resultant was dropped at a lot of hexanes, and the resultant was made to solidify. Furthermore, it remelted to the tetrahydrofuran of this congelation and this weight, and was made to solidify again by a lot of hexanes. After performing this remelting-coagulation actuation a total of 3 times, the vacuum drying of the obtained congelation was carried out at 40 degrees C for 48 hours, and the target copolymer A-5 was obtained.

[0053] Copolymer A-1 in which the radiation-curing nature constituent J-1 carried out preparation **** The radiation-curing nature constituent J-1 was obtained by carrying out 48.5 weight sections addition of the 3.0 weight sections and the ethyl lactate, and mixing to homogeneity Irgcure.369 (made in Tiba Speciality Chemicals) which are the 6.5 weight sections and a radiation radical polymerization initiator about the 10.0 weight sections and trimethylolpropane triacrylate in the polyester polyfunctional acrylate (the Toagosei make, M8100) which is a polymerization reactivity constituent to the 32.0 weight sections.

[0054] Copolymer A-2 in which the radiation-curing nature constituent J-2 carried out preparation **** The radiation-curing nature constituent J-2 was obtained by carrying out 41.6 weight sections addition of the 3.0 weight sections and the ethyl lactate, and mixing to homogeneity Irgcure.369 (made in Tiba Speciality Chemicals) which are the 11.1 weight sections and a radiation radical polymerization initiator about the 16.6 weight sections and trimethylolpropane triacrylate in the polyester polyfunctional acrylate (the Toagosei make, M8100) which is a polymerization reactivity constituent to the 27.7 weight sections.

[0055] Copolymer A-3 in which the radiation-curing nature constituent J-3 carried out preparation **** The radiation-curing nature constituent J-3 was obtained by carrying out 48.5 weight sections addition of the 3.0 weight sections and the ethyl lactate, and mixing to homogeneity Irgcure.819 (made in Tiba Speciality Chemicals) which are the 13.5 weight sections and a radiation radical polymerization initiator about the pentaerythritol thoria chestnut rate which is a polymerization reactivity constituent to the 35.0 weight sections.

[0056] Copolymer A-1 in which the radiation-curing nature constituent J-4 carried out preparation **** The radiation-curing nature constituent J-4 was obtained by carrying out 48.5 weight sections addition of the 3.0 weight sections and the ethyl lactate, and mixing to homogeneity SP170 (product made from the Asahi electrification) who are the 16.5 weight sections and a radiation cationic initiator about the polyfunctional oxirane compound (the Daicel Chemical Industries make, EPOLEAD GT 301) which is a polymerization reactivity constituent to the 32.0 weight sections.

[0057] Copolymer A-1 in which the radiation-curing nature constituent J-5 carried out preparation **** The radiation-curing nature constituent J-5 was obtained by carrying out 48.5 weight sections addition of the 3.0 weight sections and the ethyl lactate, and mixing to homogeneity Irgcure.369 (made in Tiba Speciality Chemicals) which are the 13.5 weight sections

and a radiation radical polymerization initiator about the dipentaerythritol hexaacrylate (the Nippon Kayaku make, DPFA) which is a polymerization reactivity constituent to the 35.0 weight sections.

[0058] Copolymer A-4 in which the radiation-curing nature constituent J-6 carried out preparation (example of comparison) **** The radiation-curing nature constituent J-6 was obtained by carrying out 48.5 weight sections addition of the 3.0 weight sections and the ethyl lactate, and mixing to homogeneity Irgcure.369 (made in Tiba Speciality Chemicals) which are the 6.5 weight sections and a radiation radical polymerization initiator about the 10.0 weight sections and trimethylolpropane triacrylate in the polyester polyfunctional acrylate (the Toagosei make, M8100) which is a polymerization reactivity constituent to the 32.0 weight sections.

[0059] Copolymer A-5 in which the radiation-curing nature constituent J-7 carried out preparation (example of comparison) **** The radiation-curing nature constituent J-7 was obtained by carrying out 41.6 weight sections addition of the 3.0 weight sections and the ethyl lactate, and mixing to homogeneity Irgcure.369 (made in Tiba Speciality Chemicals) which are the 11.1 weight sections and a radiation radical polymerization initiator about the 16.6 weight sections and trimethylolpropane triacrylate in the polyester polyfunctional acrylate (the Toagosei make, M8100) which is a polymerization reactivity constituent to the 27.7 weight sections.

[0060] [Example 1]

(1) The formation radiation-curing nature constituent J-2 of the formation ** lower cladding layer of optical waveguide was applied by the spin coater on the front face of a silicon substrate, and was prebaked the condition for 120 degrees C and 10 minutes using the hot plate. Subsequently, the paint film which consists of a radiation-curing nature constituent J-2 was irradiated for 30 seconds, and radiation curing of the ultraviolet rays of the wavelength of 365nm and illuminance 20 mW/cm² was carried out to it. And this hardening film was made into the lower cladding layer with a thickness of 50 micrometers by carrying out postbake on 200 degrees C and the conditions of 1 hour.

[0061] ** The paint film was formed by the spin coater on the lower cladding layer, and prebake of formation of a core part, next the radiation-curing nature constituent J-1 was carried out on 120 degrees C and the conditions for 10 minutes using the hot plate. Then, through the photo mask which has a Rhine-like pattern with a width of face of 50 micrometers, the ultraviolet rays of 2 were irradiated for 30 seconds the wavelength of 365nm, and the illuminance of 20mW/cm, and radiation curing of the paint film was carried out to the paint film with a thickness of 50 micrometers it is thin from the radiation-curing nature constituent J-1. Next, PEB was performed for the paint film which carried out radiation irradiation the condition for 100 degrees C and 1 minute. Subsequently, it was immersed into the developer which consists of a tetramethylammonium hydroxide water solution (TMAH) the substrate which has the paint film which carried out radiation hardening 1.8%, and the unexposed part of a paint film was dissolved. Then, postbake was performed on 200 degrees C and the conditions of 1 hour, and the core part which has a Rhine-like pattern with a width of face of 10 micrometers was formed.

[0062] ** **** of an up cladding layer — subsequently the radiation-curing nature constituent J-2 was applied to the top face of the lower cladding layer which has a core part by the spin coater, and it prebaked on 120 degrees C and the conditions for 10 minutes using the hot plate. Then, the up cladding layer with a thickness of 50 micrometers was formed in the paint film which consists of a radiation-curing nature constituent J-2 by irradiating the ultraviolet rays of the wavelength of 365nm, and illuminance 20 mW/cm² for 30 seconds. Then, postbake of this up cladding layer was carried out on 200 degrees C and the conditions of 6 hours.

[0063] Optical waveguide was formed by the same technique as the above mentioned technique except [all] using the constituent shown in Table 2 instead of using the constituent which described examples 2-4, the [examples 1-3 of comparison] lower cladding layer, the core part, and the up cladding layer in the example 1.

[0064] (2) The case where core height and core width of face became "O", more than it, and the following configurations about the case where the configuration of 50**5 micrometers is formed, about the core configuration (height [of 50 micrometers] x Rhine width of face of 50 micrometers) designed by technique to have carried out the precision above of the optical

waveguide configuration was made into "x." A result is shown in Table 2.

[0065] (3) transmission loss evaluation of optical waveguide --- incidence of the light with a wavelength of 824nm was carried out from the end about the optical waveguide which consists of the lower cladding layer, core part, and up cladding layer which were obtained by doing in this way. And the waveguide loss per unit length was searched for by the cutting-back method by measuring the quantity of light which carries out outgoing radiation from the other end. A result is shown in Table 2.

[0066]

[Table 1]

		J-1	J-2	J-3	J-4	J-5	J-6	J-7	J-8
(A)	A-1	32.0	-	-	32.0	35.0	-	-	32.0
	A-2	-	27.7	-	-	-	-	-	-
	A-3	-	-	35.0	-	-	-	-	-
(B)	M8100	10.0	16.6	-	-	-	10.0	16.6	-
	トリメチローノブロベンゾントリアクリレート	6.5	11.1	-	-	-	6.5	11.1	-
	ベンタエリスリトールトリアクリレート	-	-	13.5	-	-	-	-	-
	エポリードG T 301	-	-	-	16.5	-	-	-	-
	ジベンタエリスリトールキシアクリレート	-	-	-	-	13.5	-	-	-
(C)	Irgcure 369	3.0	3.0	-	-	3.0	3.0	3.0	3.0
	Irgcure 819	-	-	3.0	-	-	-	-	-
	SP170	-	-	-	3.0	-	-	-	-
(D)	乳酸エチル	48.5	41.6	48.5	48.5	48.5	48.5	41.6	48.5
その他	A-4	-	-	-	-	-	32.0	-	-
	A-5	-	-	-	-	-	-	27.7	-
	イソブチルアクリレート	-	-	-	-	-	-	-	16.5
合 計		100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

[0067]

[Table 2]

	実 施 例					比 較 例	
	1	2	3	4	5	1	2
光導波路構成							
下層クラッド層	J-2	J-2	J-2	J-2	J-7	J-7	J-7
コア部分	J-1	J-3	J-4	J-5	J-1	J-6	J-8
上層クラッド層	J-2	J-2	J-2	J-2	J-7	J-7	J-7
824 nmにおける コア・クラッド間の屈折率差 (Δn (%))	1.1	1.1	1.1	1.1	1.1	1.1	1.1
光導波路特性							
コア形状の精度	○	○	○	○	○	×	×
伝送損失[dB/cm]	0.3	0.3	0.4	0.3	0.4	>1.0	>1.0

[Translation done.]

*** NOTICES ***

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the sectional view of the optical waveguide of this invention.

[Drawing 2] (a) – (e) — a part of manufacture approach of optical waveguide — it is process drawing.

[Description of Notations]

10 Optical Waveguide

12 Substrate

13 Lower Cladding Layer

14 Thin Film for Cores

15 Core Part

16 Radiation

17 Up Cladding Layer

18 Ridge

19 Photo Mask

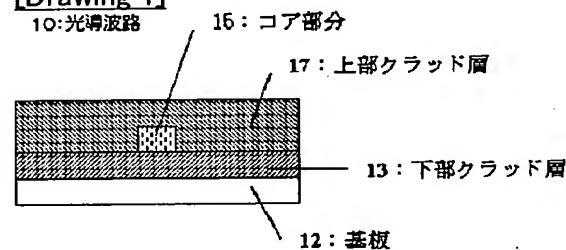
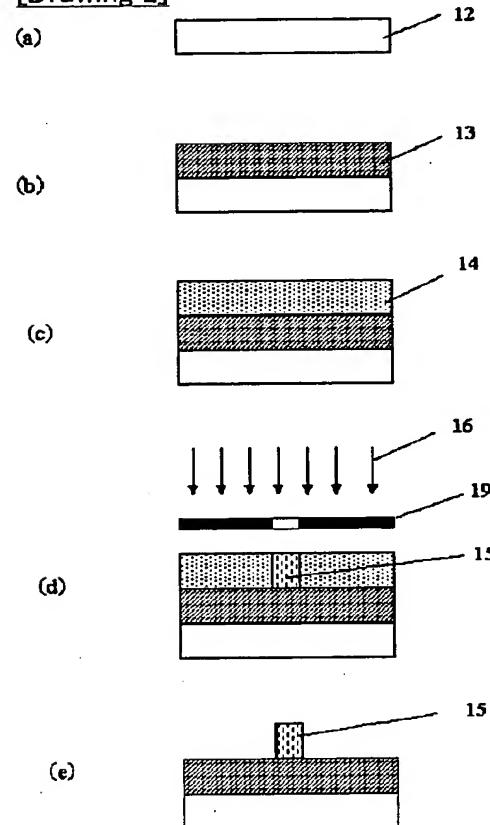
[Translation done.]

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DRAWINGS

[Drawing 1]**[Drawing 2]**

[Translation done.]

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最終頁に続く

(54) 【発明の名称】 光導波路形成用放射線硬化性組成物、光導波路ならびにその製造方法

(57) 【要約】

【課題】 伝送特性、およびその長期安定性に優れた光導波路ならびに光導波路の製造方法を提供する。

【解決手段】 下部クラッド層と、コア部分と、上部クラッド層とを含む光導波路において、下部クラッド層、コア部分および上部クラッド層の少なくとも一つが、下記 (A) ~ (C) 成分を含有してなる放射線硬化性組成物の硬化物である。

(A) (a) カルボキシル基を有するラジカル重合性化合物 (からなる構成成分が 5~50 重量%)、(b) 環状アルキル基を有し、カルボキシル基を有しないラジカル重合性化合物 (からなる構成成分が 15~60 重量%)、(c) 他のラジカル重合性化合物 (からなる構成成分が 5~80 重量%)、からなる (アルカリ可溶性を有する) 共重合体、(B) 分子中に 2 個以上の重合性反応基を有する化合物、および (C) 放射線重合開始剤

【特許請求の範囲】

【請求項1】 (A) (a) カルボキシル基を有するラジカル重合性化合物に由来する構造単位、(b) 環状アルキル基を有し、カルボキシル基を有さないラジカル重合性化合物に由来する構造単位、ならびに(c) 前記(a)および(b)以外のラジカル重合性化合物に由来する構造単位を有する共重合体。

(B) 分子中に2個以上の重合性反応基を有する化合物および

(C) 放射線重合開始剤。

を含有することを特徴とする光導波路形成用放射線硬化性組成物。

【請求項2】 (B) 成分の重合性反応基が、エチレン不飽和基であることを特徴とする請求項1記載の光導波路形成用放射線硬化性組成物。

【請求項3】 (D) 成分として、有機溶剤をさらに含有することを特徴とする請求項1記載の光導波路形成用放射線硬化性組成物。

【請求項4】 クラッド層およびコア部分の少なくとも一つが、下記(A)～(C)成分を含有する放射線硬化性組成物の硬化物からなることを特徴とする光導波路。

(A) (a) カルボキシル基を有するラジカル重合性化合物に由来する構造単位、(b) 環状アルキル基を有し、カルボキシル基を有さないラジカル重合性化合物に由来する構造単位、ならびに(c) 前記(a)および(b)以外のラジカル重合性化合物に由来する構造単位を有する共重合体

(B) 分子中に2個以上の重合性反応基を有する化合物(C) 放射線重合開始剤。

【請求項5】 クラッド層とコア部分の屈折率差が0.1%以上であることを特徴とする請求項4記載の光導波路。

【請求項6】 下部クラッド層を形成する工程と、コア部分を形成する工程と、上部クラッド層を形成する工程とを含むとともに、これらの少なくとも一つの工程が、請求項1記載の放射線硬化性組成物を放射線硬化させて形成する工程であることを特徴とする光導波路の製造方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明は、目的形状に見合った導波路形状や伝送特性に優れる光導波路を形成することができる光導波路形成用放射線硬化性組成物、それを用いて形成される光導波路ならびに光導波路の製造方法に関する。

【0002】

【従来の技術】 マルチメディア時代を迎え、光通信システムやコンピュータにおける情報処理の大容量化および高速化の要求から、光の伝送媒体として光導波路が注目されている。このような光導波路としては、石英系導波

路が代表的であり、一般に以下の工程により製造されている。

①シリコン基板上に、火炎堆積法(FHD)やCVD法等の手法によりガラス膜よりなる下部クラッド層を形成する。

②下部クラッド層上に、これと屈折率の異なる無機質の薄膜を形成し、この薄膜を反応性イオンエッチング法(RIE)を利用してパターニングすることによりコア部分を形成する。

③更に、火炎堆積法によって上部クラッド層を形成する。

しかしながら、このような石英系導波路の製造方法では、特殊な製造装置が必要であるとともに、製造時間が長くかかるなどの問題が見られた。

【0003】 そこで、本発明の発明者らは、放射線重合可能な成分を含有する組成物に、所定量の光を照射し、所定場所を放射線硬化させるとともに、未露光部を現像することによりコア部分等を形成して、伝送特性に優れる光導波路を製造する方法を提案している。このような放射線硬化性組成物を用いた光導波路の製造方法によれば、従来の石英系導波路の製造方法と比較して、所定量の光を照射した後に現像するだけで、短時間、かつ低成本で光導波路を製造できるという利点を得ることができる。しかしながら、従来に報告されている放射線硬化性組成物を用いて、上記の光導波路の製造方法を行っても、微細幅を有する光導波路を形成することが困難であったり、優れた伝送特性を有する光導波路を形成できなかつたりする場合が見られた。

【0004】

【発明が解決しようとする課題】 本発明は、以上のような事情を背景としてなされたものであって、優れた導波路形状、ならびに優れた伝送特性を有する光導波路、およびこのような光導波路を効率的に製造することができる方法を提供することを目的とする。

【0005】

【課題を解決するための手段】 本発明は、(A) (a) カルボキシル基を有するラジカル重合性化合物に由来する構造単位、(b) 環状アルキル基を有し、カルボキシル基を有さないラジカル重合性化合物に由来する構造単位、ならびに(c) 前記(a)および(b)以外のラジカル重合性化合物に由来する構造単位、(以下、「共重合体(A)」ともいう)、(B) 分子中に2個以上の重合性反応基を有する化合物、および

(C) 放射線重合開始剤、を含有することを特徴とする光導波路形成用放射線硬化性組成物(以下、「放射線硬化性組成物」ということもある)、クラッド層およびコア部分の少なくとも1つを該組成物により形成した光導波路ならびにその製造方法を提供するものである。

【0006】

【発明の実施の形態】 光導波路形成用放射線硬化性成物

共重合体(A)は、(a)カルボキシル基を有するラジカル重合性化合物、(b)環状アルキル基を有し、カルボキシル基を有しないラジカル重合性化合物、(c)前記(a)および(b)以外のラジカル重合性化合物を溶媒中でラジカル共重合することにより得ることができる。

【0007】前記カルボキシル基を有するラジカル重合性化合物(a)としては、例えばアクリル酸、メタクリル酸、クロトン酸などのモノカルボン酸；マレイン酸、フマル酸、シトラコン酸、メサコン酸、イタコン酸などのジカルボン酸；2-サクシノイルエチル(メタ)アクリレート、2-マレイノイルエチル(メタ)アクリレート、2-ヘキサヒドロフタロイルエチル(メタ)アクリレートなどのカルボキシル基およびエステル結合を有するメタクリル酸誘導体などが使用できる。これらの化合物は単独、もしくは2種以上を組み合わせて使用できる。これらの中ではアクリル酸、メタクリル酸、2-ヘキサヒドロフタロイルエチル(メタ)アクリレートが好ましく、さらに好ましくはアクリル酸やメタクリル酸である。

【0008】共重合体(A)中に占めるカルボニル基を有するラジカル重合性化合物に由来する構造単位の割合は5～50重量%であり、好ましくは10～40重量%である。この構造単位の割合が5重量%未満であると、本組成物を光照射によって硬化させアルカリ現像処理を施した場合に溶解しにくくなり、光導波路のコア部分として用いた場合、設計どおりのコア形状が得られず、十分な伝送特性が得られない。逆に50重量%を超えても、設計どおりの形状のものが得られない。

【0009】前記環状アルキル基を有し、カルボニル基を有しないラジカル重合性化合物(b)としては、例えばシクロヘキシル(メタ)アクリレート、2-メチルシクロヘキシル(メタ)アクリレート、ジシクロペニタニルオキシエチル(メタ)アクリレート、イソボルニル(メタ)アクリレート、ジシクロペニタニル(メタ)アクリレートなどを挙げることができる。これらの化合物は単独、もしくは2種以上を組み合わせて使用できる。これらの中では、ジシクロペニタニル(メタ)アクリレートが好ましい。

【0010】共重合体(A)中に占める環状アルキル基を有し、カルボニル基を有しないラジカル重合性化合物に由来する構造単位の割合は15～60重量%であり、好ましくは20～50重量%である。この割合が15重量%未満であると、得られる共重合体の分子量が十分に上がりず、20μm以上厚の本組成物の硬化膜が困難になり、希望の導波路形状を作製できない。逆に60重量%を超えると、得られる共重合体の溶剤に対する溶解性が低下し、共重合体を調製する際に問題が生ずる。

【0011】前記他のラジカル重合性化合物(c)は、主として共重合体(A)の機械的特性や屈折率を適度に

コントロールする目的で使用する。このような他のラジカル重合性化合物(c)としては、好ましくは(メタ)アクリル酸アルキルエステル類、(メタ)アクリル酸アリールエステル類、ジカルボン酸ジエステル類、芳香族ビニル類、共役ジオレフィン類、ニトリル基含有重合性化合物、塩素含有重合性化合物、アミド結合含有重合性化合物、脂肪酸ビニル類などを挙げることができる。具体的には、メチル(メタ)アクリレート、エチル(メタ)アクリレート、イソプロピル(メタ)アクリレート、n-ブチル(メタ)アクリレート、sec-ブチル(メタ)アクリレート、t-ブチル(メタ)アクリレートなどの(メタ)アクリル酸アルキルエステル；フェニル(メタ)アクリレート、ベンジル(メタ)アクリレートなどの(メタ)アクリル酸アリールエステル；マレイン酸ジエチル、フマル酸ジエチル、イタコン酸ジエチルなどのジカルボン酸ジエステル；スチレン、α-メチルスチレン、m-メチルスチレン、p-メチルスチレン、ビニルトルエン、p-メトキシスチレンなどの芳香族ビニル類；1,3-ブタジエン、イソブレン、1,4-ジメチルブタジエンなどの共役ジオレフィン類、アクリロニトリル、メタクリロニトリルなどのニトリル基含有重合性化合物；塩化ビニル、塩化ビニリデンなどの塩素含有重合性化合物；アクリルアミド、メタクリルアミドなどのアミド結合含有重合性化合物；酢酸ビニルなどの脂肪酸ビニル類を用いることができる。これらの化合物は単独、もしくは2種以上を組み合わせて用いることができ、これらのうち、メチル(メタ)アクリレート、n-ブチル(メタ)アクリレート、スチレン、α-メチルスチレンなどが特に好ましい。共重合体(A)中に占める(a)および(b)以外のラジカル重合性化合物に由来する構造単位の割合は5～80重量%であり、好ましくは20～70重量%である。

【0012】共重合体(A)を合成する際に用いられる重合溶媒としては、例えばメタノール、エタノール、エチレングリコール、ジエチレングリコール、プロピレングリコールなどのアルコール類；テトラヒドロフラン、ジオキサンなどの環状エーテル類；エチレングリコールモノメチルエーテル、エチレングリコールモノエチルエーテル、エチレングリコールジメチルエーテル、エチレングリコールジエチルエーテル、ジエチレングリコールモノメチルエーテル、ジエチレングリコールモノエチルエーテル、ジエチレングリコールジメチルエーテル、ジエチレングリコールジエチルエーテル、ジエチレングリコールエチルエーテルアセテート、ジエチレングリコールエチルエーテルアセテート、プロピレングリコールエチルエーテルアセテートなどの多価アルコールのアルキルエーテル類；トルエン、キシリ

ンなどの芳香族炭化水素類；アセトン、メチルエチルケトン、メチルイソブチルケトン、シクロヘキサン、4-ヒドロキシ-4-メチル-2-ペントノン、ジアセトアルコールなどのケトン類；酢酸エチル、酢酸ブチル、乳酸エチル、2-ヒドロキシプロピオン酸エチル、2-ヒドロキシ-2-メチルプロピオン酸エチル、2-ヒドロキシ-2-メチルプロピオン酸エチル、エトキシ酢酸エチル、ヒドロキシ酢酸エチル、2-ヒドロキシ-3-メチルブタン酸メチル、3-メトキシプロピオン酸メチル、3-メトキシプロピオン酸エチル、3-エトキシプロピオン酸エチル、3-エトキシプロピオン酸メチルなどのエステル類が挙げられる。これらのうち、環状エーテル類、多価アルコールのアルキルエーテル類、多価アルコールのアルキルエーテルアセテート類、ケトン類、エステル類などが好ましい。

【0013】また、ラジカル共重合における重合触媒としては、通常のラジカル重合開始剤が使用でき、例えば2, 2'-アゾビスイソブチロニトリル、2, 2'-アゾビス-(2, 4-ジメチルバレロニトリル)、2, 2'-アゾビス-(4-メトキシ-2'-ジメチルバレロニトリル)などのアゾ化合物；ベンゾイルペルオキシド、ラウロイルペルオキシド、t-ブチルペルオキシバレート、1, 1'-ビス-(t-ブチルペルオキシシクロヘキサンなどの有機過酸化物、および過酸化水素などを挙げることができる。過酸化物をラジカル重合開始剤に使用する場合、還元剤を組み合わせてレドックス型の開始剤としてもよい。得られる共重合体(A)の好ましい平均分子量は3, 000~100, 000である。この分子量はゲルパークションクロマトグラフィ(GPC)によって求められるポリスチレン換算で定義される。分子量が3, 000未満であると、基板上に本組成物を所定の膜厚で塗工することが困難になる。逆に、分子量が100, 000を超えると、本組成物で光導波路を形成する際、目的の導波路形状が得られない場合がある。

【0014】本発明の組成物を構成する分子中に2個以上の重合性反応基を有する化合物(B)は、熱重合、および/または光重合する化合物であり、以下に示されるような化合物を例示することができる。

分子中に2個以上のエチレン性不飽和基を有する化合物；(メタ)アクリロイル基、またはビニル基を分子中に2個以上含有する化合物を使用することができる。このような化合物としては、例えばエチレングリコールジ(メタ)アクリレート、テトラエチレングリコールジ(メタ)アクリレート、ポリエチレングリコールジ(メタ)アクリレート、1, 4-ブタンジオールジ(メタ)アクリレート、1, 6-ヘキサンジオールジ(メタ)アクリレート、ネオペンチルグリコールジ(メタ)アクリレート、トリス(2-ヒドロキシエチル)イソシアヌレートジ(メタ)アクリレート、ビス(ヒドロキシメチ

ル)トリシクロデカンジ(メタ)アクリレート、ビスフェノールAのエチレンオキサイドまたはプロピレンオキサイドの付加体であるジオールジ(メタ)アクリレート、水添ビスフェノールAのエチレンオキサイドまたはプロピレンオキサイドの付加体であるジオールジ(メタ)アクリレート、ビスフェノールAのジグリシジルエーテルに(メタ)アクリレートを付加させたエポキシ(メタ)アクリレート、ポリオキシアルキレン化ビスフェノールAのジアクリレート等が挙げられる。さらに分子中に3個以上の(メタ)アクリロイル基を含有する(メタ)アクリレートとしては、3個以上の水酸基を有する多価アルコールに3モル以上の(メタ)アクリル酸がエステル結合した化合物、例えばトリメチロールプロパントリ(メタ)アクリレート、ベンタエリスリトールトリ(メタ)アクリレート、トリメチロールプロパントリオキシエチル(メタ)アクリレート、トリス(2-ヒドロキシエチル)イソシアヌレートトリ(メタ)アクリレート、ジベンタエリスリトールヘキサ(メタ)アクリレート等が挙げられる。また、主鎖にポリエーテル、ポリエステル、ポリウレタン骨格を有するポリエーテルアクリルオリゴマー、ポリエステルアクリルオリゴマー、ポリウレタンアクリルオリゴマー、あるいはポリエポキシアクリルオリゴマーも使用することができる。

【0015】これらの市販品としては、ユピマーUV SA1002、SA2007(以上、三菱化学製)、ビスコート#195、#230、#215、#260、#295、#300、#335HP、#360、#400、#540、#700、3PA、GPT(以上、大阪有機化学工業製)、ライトアクリレート4EG-A、9EG-A、NP-A、DCP-A、BP-4EA、BP-4PA、PE-3A、PE-4A、DPE-6A(以上、共栄社化学製)、KAYARAD MANDA、HX-220、HX-620、R-551、R-712、R-604、R-684、PET-30、GPO-303、TMPTA、DPHA、D-310、D-330、DPCA-20、-30、-60、-120(以上、日本化薬製)、アロニックスM208、M210、M215、M220、M240、M305、M309、M310、M315、M325、M400、M1200、M6100、M6200、M6250、M7100、M8030、M8060、M8100、M8530、M8560、M9050(以上、東亞合成製)、リポキシVR-77、VR-60、VR-90(以上、昭和高分子製)、Ebecry181、83、600、629、645、745、754、767、701、755、705、770、800、805、810、830、450、1830、1870(以上、ダイセルUCB製)、ビームセット575、551B、502H、102(以上、荒川化学製)等が挙げられる。

【0016】分子中に2個以上の環状エーテル類を有す

る化合物；オキシラン化合物、オキセタン化合物、オキソラン化合物などのうち、分子中に2個以上の環状エーテルを有する化合物を使用することができる。例えばオキシラン化合物類として3, 4-エポキシシクロヘキシルメチル-3', 4'-エポキシシクロヘキサンカルボキシレート、2-(3, 4-エポキシシクロヘキシル-5, 5-スピロー-3, 4-エポキシ)シクロヘキサン-メタージオキサン、ビス(3, 4-エポキシシクロヘキシルメチル)アジペート、ビス(3, 4-エポキシ-6-メチルシクロヘキシルメチル)アジペート、3, 4-エポキシ-6-メチルシクロヘキシル-3', 4'-エポキシ-6'-メチルシクロヘキサンカルボキシレート、メチレンビス(3, 4-エポキシシクロヘキサン)、ジシクロヘンタジエンジエポキサイド、エチレングリコールのジ(3, 4-エポキシシクロヘキシルメチル)エーテル、エチレンビス(3, 4-エポキシシクロヘキサンカルボキシレート)、エポキシ化テトラベンジルアルコール、ラクトン変性3, 4-エポキシシクロヘキシルメチル-3', 4'-エポキシシクロヘキサンカルボキシレート、ラクトン変性エポキシ化テトラヒドロベンジルアルコール、シクロヘキセンオキサイド、ビスフェノールAジグリシジルエーテル、ビスフェノールFジグリシジルエーテル、ビスフェノールSジグリシジルエーテル、水添ビスフェノールAジグリシジルエーテル、水添ビスフェノールFジグリシジルエーテル、水添ビスフェノールADジグリシジルエーテル、臭素化ビスフェノールAジグリシジルエーテル、臭素化ビスフェノールFジグリシジルエーテル、臭素化ビスフェノールSジグリシジルエーテル、エポキシノボラック樹脂、1, 4-ブタンジオールジグリシジルエーテル、1, 6-ヘキサンジオールジグリシジルエーテル、グリセリントリグリシジルエーテル、トリメチロールプロパントリグリシジルエーテル、ポリエチレングリコールジグリシジルエーテル、ポリプロピレングリコールジグリシジルエーテル類；エチレングリコール、プロピレングリコール、グリセリンなどの脂肪族多価アルコールに1種または2種以上のアルキレンオキサイドを付加することにより得られるポリエーテルポリオールのポリグリシジルエーテル類；脂肪族長鎖二塩基酸のジグリシジルエステル類；脂肪族高級アルコールのモノグリシジルエーテル類；フェノール、クレゾール、ブチルフェノールまたはこれらにアルキレンオキサイドを付加して得られるポリエーテルアルコールのモノグリシジルエーテル類；高級脂肪酸のグリシジルエステル類；エポキシ化大豆油、エポキシステアリン酸ブチル、エポキシステアリン酸オクチル、エポキシ化アマニ油などを挙げることができる。オキセタン化合物として、3, 7-ビス(3-オキセタニル)-5-オキサノナン、3, 3'-(1, 3-(2-メチレニル)プロパンジイルビス(オキシメチレン))ビス-(3-エチルオキセタン)、1, 4-ビス[(3-

エチル-3-オキセタニルメトキシ)メチル]ベンゼン、1, 2-ビス[(3-エチル-3-オキセタニルメトキシ)メチル]エタン、1, 3-ビス[(3-エチル-3-オキセタニルメトキシ)メチル]プロパン、エチレングリコールビス(3-エチル-3-オキセタニルメチル)エーテル、ジシクロヘンテニルビス(3-エチル-3-オキセタニルメチル)エーテル、トリエチレングリコールビス(3-エチル-3-オキセタニルメチル)エーテル、テトラエチレングリコールビス(3-エチル-3-オキセタニルメチル)エーテル、トリシクロデカジメチレン(3-エチル-3-オキセタニルメチル)エーテル、トリメチロールプロパントリス(3-エチル-3-オキセタニルメチル)エーテル、1, 4-ビス(3-エチル-3-オキセタニルメトキシ)ブタン、1, 6-ビス(3-エチル-3-オキセタニルメトキシ)ヘキサン、ペンタエリスリトールトリス(3-エチル-3-オキセタニルメチル)エーテル、ペンタエリスリトールテトラキス(3-エチル-3-オキセタニルメチル)エーテルなどを例示することができ、これらは1種単独あるいは2種以上を組み合わせて用いることができる。

【0017】これらの市販品としては、エポライト40E、100E、70P、1500NP、100MF、4000、3002(以上、共栄社化学製)、セロキサイド2021、2081、GT301、GT401、エポリードCDM、PB3600、エポフレンドA1005、A1010、A1020(以上、ダイセル化学工業製)、デナコール611、612、512、521、411、421、313、321(以上、ナガセ化成製)等が挙げられる。

【0018】また、前記したエチレン性不飽和基、および環状エーテルの両反応性基を分子中にそれぞれ少なくとも1個以上含有する化合物であってもよい。例えば、グリシジル(メタ)アクリレート、ビニルシクロヘキセンオキサイド、4-ビニルエポキシシクロヘキサン、3, 4-エポキシシクロヘキシルメチル(メタ)アクリレートなどが挙げられる。これらの化合物(B)は、単独、または2種以上で用いてもよく、特にエチレン性不飽和基を分子中に2個以上含有する化合物を使用することが好ましい。共重合体(A)100重量部に対して、好ましくは30~150重量部、より好ましくは50~130重量部である。30重量部未満であると、光導波路を形成する際、目的の導波路形状が得られない場合があり、150重量部を超えると、共重合体(A)との相溶性が悪くなり、硬化物表面に膜荒れを生じることがある。

【0019】本発明の組成物を構成する放射線重合開始剤(C)は、放射線によって前記した化合物(B)を重合しうる活性種を発生できる開始剤である。ここで放射線とは、例えば赤外線、可視光線、紫外線およびX線、

電子線、 α 線、 β 線、 γ 線のような電離放射線を意味する。従って、成分(C)である放射線重合開始剤を必要とし、必要に応じて、さらに光増感剤を添加する。放射線重合開始剤としては、光照射により分解してラジカルを発生するもの(放射線ラジカル重合開始剤)、カチオンを発生するもの(放射線カチオン重合開始剤)に大別できる。

【0020】放射線ラジカル重合開始剤としては、例えばアセトフェノン、アセトフェノンベンジルケタール、1-ヒドロキシシクロヘキシルフェニルケトン、2, 2-ジメトキシ-2-フェニルアセトフェノン、キサントン、フルオレノン、ベンズアルデヒド、フルオレン、アントラキノン、トリフェニルアミン、カルバゾール、3-メチルアセトフェノン、4-クロロベンゾフェノン、4, 4'-ジメトキシベンゾフェノン、4, 4'-ジアミノベンゾフェノン、ミヒラーケトン、ベンゾインプロピルエーテル、ベンゾインエチルエーテル、ベンジルジメチルケタール、1-(4-イソプロピルフェニル)-2-ヒドロキシ-2-メチルプロパン-1-オン、2-ヒドロキシ-2-メチル-1-フェニルプロパン-1-

[R¹²a R¹³b R¹⁴c R¹⁵d]

〔式中、カチオンはオニウムイオンであり、WはS、Se、Te、P、As、Sb、Bi、O、I、Br、ClまたはN≡Nであり、R¹²、R¹³、R¹⁴およびR¹⁵は同一または異なる有機基であり、a、b、cおよびdはそれぞれ0~3の整数であって、(a+b+c+d)はWの値数に等しい。Mは、ハロゲン化物錯体[MX_{n+m}]の中心原子を構成する金属またはメタロイドであり、例えばB、P、As、Sb、Fe、Sn、Bi、Al、Ca、In、Ti、Zn、Sc、V、Cr、Mn、Coなどである。Xは例えばF、Cl、Br等のハロゲン原子であり、mはハロゲン化物錯体イオンの正味の電荷であり、nはMの原子価である。〕

一般式(1)においてオニウムイオンの具体例としては、ジフェニルヨードニウム、4-メトキシジフェニルヨードニウム、ビス(4-メチルフェニル)ヨードニウム、ビス(4-tert-ブチルフェニル)ヨードニウム、ビス(ドデシルフェニル)ヨードニウム、トリフェニルスルホニウム、ジフェニル-4-チオフェノキシフェニルスルホニウム、ビス[4-(ジフェニルスルfonylo)-フェニル]スルフィド、ビス[4-(ジ(4-(2-ヒドロキシエチル)フェニル)スルホニオ)-エニル]スルフィド、η⁵-2, 4-(シクロペニタジエニル)[1, 2, 3, 4, 5, 6-η]-(メチルエチル)-ベンゼン]-鉄(1+)等が挙げられる。

【0023】上記一般式(1)中における陰イオン(MX_{n+m})の具体例としては、テトラフルオロボレート(BF₄⁻)、ヘキサフルオロホスフェート(PF₆⁻)、ヘキサフルオロアンチモネート(SbF₆⁻)、ヘキサフルオロアルセネート(AsF₆⁻)、ヘキサクロロアンチ

オン、チオキサントン、ジエチルチオキサントン、2-イソプロピルチオキサントン、2-クロロチオキサントン、2-メチル-1-[4-(メチルチオ)フェニル]-2-モルホリノ-プロパン-1-オン、2, 4, 6-トリメチルベンゾイルジフェニルfosfinオキサイド、ビス-(2, 6-ジメトキシベンゾイル)-2, 4, 4-トリメチルベンチルfosfinオキサイド等が挙げられる。

【0021】放射線ラジカル重合開始剤の市販品としては、例えばIrgacure 184、369、651、500、819、907、784、2959、CGI 1700、CGI 1750、CGI 11850、CG 24-61、Darocur 1116、1173(以上、チバ・スペシャリティ・ケミカルズ製)、Lucirin TPO、TPO-L(以上、BASF製)、ユベクリルP 36(UCB製)等が挙げられる。

【0022】放射線カチオン重合開始剤としては、下記一般式(1)で表される構造を有するオニウム塩を挙げることができる。このオニウム塩は、光を受けることによりルイス酸を放出する化合物である。

W] ^m [MX_{n+m}] ⁻ⁿ (1)

モネート(SbCl₆⁻)などが挙げられる。放射線カチオン重合開始剤として使用することができるオニウム塩として、前記一般式(27)において、[MX_{n+m}]の代わりに一般式:

[MX_n(OH)⁻]

(ここで、M、Xおよびnは一般式(1)に関し定義の通りである。)で表される陰イオン、過塩素酸イオン(ClO₄⁻)、トリフルオロメタンスルfony酸イオン(CF₃SO³⁻)、フルオロスルfony酸イオン(FSO₃⁻)、トルエンスルfony酸イオン、トリニトロベンゼンスルfony酸イオン、トリニトロトルエンスルfony酸イオンなどの他の陰イオンを有するオニウム塩が挙げられる。

【0024】放射線カチオン重合開始剤の市販品としては、例えばUV I-6950、UV I-6970、UV I-6974、UV I-6990(以上、ユニオンカーバイド社)、アデカオプトマーSP-150、SP-151、SP-170、SP-171(以上、旭電化工業(株))、Irgacure 261(以上、チバガイギー社)、CI-2481、CI-2624、CI-2639、CI-2064(以上、日本曹達(株))、CD-1010、CD-1011、CD-1012(以上、サートマー社)、DTS-102、DTS-103、NAT-103、NDS-103、TPS-102、TPS-103、MDS-103、MPI-103、BBI-101、BBI-102、BBI-103(以上、みどり化学(株))、Degacure K126(デグサ社製)などが挙げられる。前記の放射線重合開始剤は、1種単独、あるいは2種以上のものを組み

合わせて(C)成分を構成することができる。

【0025】本発明の放射線硬化性組成物における

(C)成分の含有割合は、成分(A)と(B)の合計量100重量部としたときに、通常0.1～20重量部であることが好ましく、0.2～10重量部であることが特に好ましい。(C)成分の含有割合が0.1重量部未満であると、硬化が十分に進行せず、光導波路の伝送特性で問題を生ずることがある。一方、20重量部を超えると、開始剤が長期の伝送特性に悪影響を及ぼす可能性がある。

【0026】また、放射線硬化性組成物において、上述した放射線重合開始剤と併用して光増感剤を配合することも好ましい。この理由は、光増感剤を併用することにより、光等のエネルギー線をより効果的に吸収することができるためである。このような光増感剤としては、チオキサントン、ジエチルチオキサントンおよびチオキサントンの誘導体；アントラキノン、プロムアントラキノンおよびアントラキノンの誘導体；アントラゼン、プロムアントラゼンおよびアントラゼン誘導体；ペリレンおよびペリレンの誘導体；キサントン、チオキサントンおよびチオキサントンの誘導体；クマリンおよびケトクマリン等を挙げることができる。これらの光増感剤は、開始剤の種類に応じて適した増感剤を選択する必要がある。

【0027】本発明の放射線硬化性組成物には、前記の成分以外に、必要に応じて本発明の放射線硬化性組成物の特性を損なわない範囲で、例えば分子中に1個の重合性反応基を含有する化合物や高分子樹脂、例えば、エポキシ樹脂、アクリル樹脂、ポリアミド樹脂、ポリアミドイミド樹脂、ポリウレタン樹脂、ポリブタジエン樹脂、ポリクロロブレン樹脂、ポリエーテル樹脂、ポリエステル樹脂、スチレン-ブタジエンブロック共重合体、石油樹脂、キシレン樹脂、ケトン樹脂、セルロース樹脂、フッ素系ポリマー、シリコーン系ポリマーを配合することができる。

【0028】さらにまた、上記成分以外に必要に応じて各種添加剤として、例えば酸化防止剤、紫外線吸収剤、光安定剤、シランカップリング剤、塗面改良剤、熱重合禁止剤、レベリング剤、界面活性剤、着色剤、保存安定剤、可塑剤、滑剤、フィラー、微粒子、老化防止剤、濡れ性改良剤、帯電防止剤等を必要に応じて配合することができる。ここで、酸化防止剤としては、例えばIrganox1010、1035、1076、1222(以上、チバ・スペシャルティ・ケミカルズ製)、Antigen P、3C、FR、スマライザー(住友化学工業製)等が挙げられ、紫外線吸収剤としては、例えばTinuvin P、234、320、326、327、328、329、213(以上、チバ・スペシャルティ・ケミカルズ製)、Seesorb 102、103、110、501、202、712、704(以上、シプロ

化成製)等が挙げられ、光安定剤としては、例えばTinuvin 292、144、622LD(以上、チバ・スペシャルティ・ケミカルズ製)、サノールLS770(三共製)、Sumisorb TM-061(住友化学工業製)等が挙げられ、シランカップリング剤としては、例えばγ-アミノプロピルトリエトキシシラン、γ-メルカブトプロピルトリメトキシシラン、γ-メタアクリロキシプロピルトリメトキシシラン、市販品として、SH6062、6030(以上、東レ・ダウコーニング・シリコーン製)、KBE903、603、403(以上、信越化学工業製)等が挙げられ、塗面改良剤としては、例えばジメチルシロキサンポリエーテル等のシリコーン添加剤が挙げられ、市販品としてはDC-57、DC-190(以上、ダウコーニング製)、SH-28PA、SH-29PA、SH-30PA、SH-190(以上、東レ・ダウコーニング・シリコーン製)、KF351、KF352、KF353、KF354(以上、信越化学工業製)、L-700、L-7002、L-7500、FK-024-90(以上、日本ユニカー製)等が挙げられる。

【0029】本発明の放射線硬化性組成物は、さらに(D)成分として、有機溶媒を含有することが好ましい。有機溶媒を添加することにより、放射線硬化性組成物の保存安定性が向上するとともに、適当な粘度を得ることができるために、均一な厚さを有する光導波路を形成することができる。

【0030】有機溶媒の種類としては、本発明の目的、効果を損なわない範囲で選ぶことができるが、通常、大気圧下での沸点が50～200℃の範囲内の値を有する有機化合物であって、各構成成分を均一に溶解させる有機化合物であることが好ましい。具体的には、成分

(A)の共重合体を調製する際に使用する有機溶剤を用いることができる。好ましい有機溶剤としては、アルコール類、エステル類、およびケトン類が挙げられ、より好ましい有機溶媒としては、プロピレンギリコールモノメチルエーテル、乳酸エチル、メチルイソブチルケトン、メチルアミルケトン、トルエン、キシレン、およびメタノールからなる群から選択される少なくとも1つの溶剤が挙げられる。

【0031】有機溶媒の含有量は、成分(A)から(C)の総重量100重量部としたときに、10～200重量部の範囲内の値とすることが好ましい。かかる有機溶媒の添加量が10重量部未満となると、放射線硬化性組成物の粘度調整が困難となる場合があるためであり、一方、有機溶媒の添加量が200重量部を超えると、十分な厚さを有する光導波路等を形成することが困難となる場合があるためである。

【0032】本発明の放射線硬化性組成物は、使用する部位、すなわちクラッド層またはコア部分に必要な屈折率とするために、上記(A)成分、(B)成分の種類、

配合量等を適宜選択する。本発明の放射線硬化性組成物を調製する際に、その粘度を、1~10,000 cps (25°C) の範囲内の値とすることが好ましく、5~8,000 cps (25°C) の範囲内の値とすることがより好ましく、10~5,000 cps (25°C) の範囲内の値とすることがさらに好ましい。

【0033】光導波路

図1は、本発明の放射線硬化性組成物を適用して構成した光導波路の基本的構成を示す断面図である。この図1に示すように、光導波路は、紙面に直角方向（奥行き方向）に伸びる基板12と、この基板12の表面上に形成された下部クラッド層13と、この下部クラッド層13上に形成された、特定の幅を有するコア部分15と、このコア部分15を含む下部クラッド層13上に積層して形成された上部クラッド層17と、を含んで構成されている。そして、コア部分15は、導波路損失が少なくなるように、その側部を含めて、下部クラッド層13および上部クラッド層17により被覆しており、全体として埋設された状態である。

【0034】以上のような構成の光導波路において、下部クラッド層、上部クラッド層、およびコア部分の厚さはそれぞれ特に制限されるものではないが、例えば、下部クラッド層の厚さを1~200 μm、コア部分の厚さを3~200 μm、上部クラッド層の厚さを1~200 μmの範囲内の値とすることが好ましい。また、コア部分の幅についても特に限定されるものではないが、例えば、1~200 μmの範囲内の値とすることが好ましい。

【0035】また、コア部分の屈折率を、下部および上部クラッド層のいずれの屈折率よりも大きくすることが必要である。したがって、波長400~1,600 nmの光に対して、コア部分の屈折率を1.420~1.650の範囲内の値とするとともに、下部クラッド層および上部クラッド層の屈折率をそれぞれ1.400~1.648の範囲内の値とすることが好ましい。また、コア部分とクラッド層の屈折率差が0.1%以上離れていることが好ましく、特にコア部分の屈折率を、クラッド層の屈折率よりも少なくとも0.1%大きい値とすることが好ましい。本発明の光導波路は、上記クラッド層およびコア部分の少なくとも1つが、本発明の放射線硬化性組成物の硬化物からなるものである。本発明の放射線硬化性組成物の硬化物により形成されないクラッド層およびコア部分は、ポリイミド、ポリアクリレート、ポリカーボネート、ポリシロキサンなどにより形成することができる。

【0036】光導波路は、図2に示すような工程を経て形成される。すなわち、下部クラッド層13、コア部分15および上部クラッド層（図示せず。）を、いずれも、それらの層を形成するための放射線硬化性組成物を塗工したのち、放射線硬化することにより形成すること

が好ましい。なお、以下の形成例では、下部クラッド層、コア部分および上部クラッド層を、それぞれ硬化後において屈折率が異なる硬化物が得られる放射線硬化性組成物である下層用組成物、コア用組成物、および上層用組成物から形成することを想定して、説明する。そして、屈折率の差が適宜の大きさとなるような二種または三種の放射線硬化性組成物を用い、最も高い屈折率の硬化膜を与える放射線硬化性組成物をコア用組成物とし、他の放射線硬化性組成物を下層用組成物および上層用組成物として用いることが好ましい。ただし、下層用組成物と上層用組成物とは同一の放射線硬化性組成物であつてもよく、通常は同一の組成物であることが、経済的に有利であり、製造管理も容易となることからより好ましい。

【0037】①基板の準備

まず、図2(a)に示すように、平坦な表面を有する基板12を用意する。この基板12の種類としては、特に制限されるものではないが、例えば、シリコン基板やガラス基板等を用いることができる。

【0038】②下部クラッド層の形成工程

用意した基板12の表面に、下部クラッド層13を形成する工程である。具体的には、図2(b)に示すように、基板12の表面に、下層用組成物を塗布し、乾燥またはプリベークさせて下層用薄膜を形成する。そして、この下層用薄膜に、放射線を照射することにより硬化させて、下部クラッド層13を形成することができる。なお、下部クラッド層13の形成工程では、薄膜の全面に放射線を照射し、その全体を硬化することが好ましい。

【0039】ここで、下層用組成物を塗布方法としては、スピンドルコート法、ディッピング法、スプレー法、バーコート法、ロールコート法、カーテンコート法、グラビア印刷法、シルクスクリーン法、またはインクジェット法等の方法を用いることができる。このうち、特に均一な厚さの下層用薄膜が得られることから、スピンドルコート法を採用することがより好ましい。また、下層用組成物のレオロジー特性を塗布方法に適切に対応したものとするために、各種レベリング剤、チクソ付与剤、フィラー、有機溶媒、界面活性剤等を必要に応じて配合することが好ましい。また、下層用組成物からなる下層用薄膜は、塗布後、有機溶剤などを除去する目的で50~200°Cの温度でプリベークすることが好ましい。なお、下部クラッド層の形成工程における塗布方法や、レオロジー特性の改良等については、後述するコア部分の形成工程や、上部クラッド層の形成工程においてもあてはまる内容である。

【0040】また、下部クラッド層を形成する際の放射線の照射量についても、特に制限されるものでは無いが、波長200~390 nm、照度0.1~500 mW/cm²の放射線を、照射量が10~5,000 mJ/cm²となるように照射して、露光することが好まし

い。ここに、照射される放射線の種類としては、可視光、紫外線、赤外線、X線、 α 線、 β 線、 γ 線等を用いることができるが、特に紫外線が好ましい。そして、放射線（紫外線）の照射装置としては、例えば、高圧水銀ランプ、低圧水銀ランプ、メタルハライドランプ、エキシマランプ等を用いることが好ましい。また、露光後に、塗膜全面が十分硬化するように、さらに加熱処理（以下、「ポストベーク」という。）を行うことが好ましい。この加熱条件は、放射線硬化性組成物の配合組成、添加剤の種類等により変わるが、通常、30～40℃、好ましくは50～300℃で、例えば5分間～72時間の加熱条件とすれば良い。なお、下部クラッド層の形成工程における放射線の照射量、種類、および放射線（紫外線）の照射装置等については、後述するコア部分の形成工程や、上部クラッド層の形成工程においてもあてはまる内容である。

【0041】③コア部分の形成

次に、この下部クラッド層13上に、図2(c)に示すように、コア用組成物を塗布し、乾燥またはさらにプリベークさせてコア用薄膜14を形成する。その後、図2(d)に示すように、コア用薄膜14の上面に対して、所定のパターンに従って、例えば所定のラインパターンを有するフォトマスク19を介して放射線16の照射を行うことが好ましい。これにより、放射線が照射された箇所のみが硬化するので、それ以外の未硬化の部分を現像除去することにより、図2(e)に示すように、下部クラッド層13上に、パターニングされた硬化膜よりなるコア部分15を形成することができる。

【0042】また、コア部分15を形成するためのコア用薄膜14に対する放射線16の照射は、所定のパターンを有するフォトマスク19に従って行われた後、現像液により未露光部分を現像することにより、未硬化の不要な部分が除去され、これによってコア部分15が形成される。このように所定のパターンに従って放射線の照射を行う方法としては、放射線の透過部と非透過部とかなるフォトマスクを用いる方法に限られず、例えば、以下に示すa～cの方法が挙げられる。

a. 液晶表示装置と同様の原理を利用した、所定のパターンに従って放射線透過領域と放射線不透過領域となりマスク像を電気光学的に形成する手段を利用する方法。

b. 多数の光ファイバーを束ねてなる導光部材を用い、この導光部材における所定のパターンに対応する光ファイバーを介して放射線を照射する方法。

c. レーザ光、あるいはレンズ、ミラー等の集光性光学系により得られる収束性放射線を走査させながら放射線硬化性組成物に照射する方法。

なお、露光後、露光部分の硬化を促進させるために、加熱処理（以下、「PEB」という。）を行うことが好ましい。その加熱条件は、放射線硬化性組成物の配合組

成、添加剤の種類等により変わるが、通常、30～200℃、好ましくは50～150℃である。

【0043】このようにして所定のパターンに従ってパターン露光し、選択的に硬化させた薄膜に対しては、硬化部分と未硬化部分との溶解性の差を利用して、現像処理することができる。したがって、パターン露光後、未硬化部分を除去するとともに、硬化部分を残存させることにより、結果として、コア部分を形成することができる。

【0044】ここで、現像液としては、有機溶媒、あるいは水酸化ナトリウム、水酸化カリウム、炭酸ナトリウム、ケイ酸ナトリウム、メタケイ酸ナトリウム、アンモニア、エチルアミン、n-ブロピルアミン、ジエチルアミン、ジ-n-ブロピルアミン、トリエチルアミン、メチルジエチルアミン、N-メチルピロリドン、ジメチルエタノールアミン、トリエタノールアミン、テトラメチルアンモニウムヒドロキシド、テトラエチルアンモニウムヒドロキシド、コリン、ピロール、ビペリジン、1,8-ジアザビシクロ[5.4.0]-7-ウンデセン、1,5-ジアザビシクロ[4.3.0]-5-ノナンなどのアルカリ類からなるアルカリ水溶液等を用いることができる。また、アルカリ水溶性を使用する場合、その濃度を、通常0.05～2.5重量%、好ましくは0.1～3.0重量%の範囲内の値とすることが好ましい。なお、このようなアルカリ水溶液に、メタノール、エタノールなどの水溶性有機溶媒や界面活性剤などを適当量添加して、現像液として使用することも好ましい。

【0045】また、現像時間は、通常30～600秒間であり、また現像方法は液盛り法、ディッピング法、シャワー現像法などの公知の方法を採用することができる。現像液として有機溶媒を用いた場合はそのまま風乾することにより、また、アルカリ水溶液を用いた場合には流水洗浄を、例えば30～90秒間行い、圧縮空気や圧縮窒素等で風乾させることによって表面上の水分を除去することにより、パターン状被膜が形成される。次いで、パターニング部をさらに硬化するために、ホットプレートやオーブンなどの加熱装置により、例えば30～400℃の温度で5～600分間ポストベーク処理し、硬化されたコア部分が形成されることになる。

【0046】④上部クラッド層の形成

次いで、コア部分15が形成された下部クラッド層13の表面に、上層用組成物を塗布し、乾燥またはプリベークさせて上層用薄膜を形成する。この上層用薄膜に対し、放射線を照射して硬化させることにより、図1に示したように上部クラッド層17を形成することができる。また、放射線の照射によって得られる上部クラッド層は、必要に応じて、さらに上述したポストベークすることが好ましい。ポストベークすることにより、硬度および耐熱性に優れた上部クラッド層を得ることができる。

【0047】

【実施例】以下、本発明を実施例により具体的に説明するが、本発明はこれら実施例に限定されるものではない。

【0048】[放射線硬化性組成物の調製]

コア部分用共重合体(A)の調製例1

ドライアイス/メタノール還流器の付いたフラスコを窒素置換した後、重合開始剤として2, 2'-アゾビスイソブチロニトリルを1. 3 g、有機溶剤として乳酸エチルを53. 8 gを仕込み、重合開始剤が溶解するまで攪拌した。引き続いて、メタクリル酸6. 7 g、ジシクロペニタニルメタクリレート15. 7 g、スチレン9. 0 g、およびn-ブチルアクリレート13. 5 gを仕込んだ後、緩やかに攪拌を始めた。その後、溶液の温度を80°Cに上昇させ、この温度で4時間重合を行った。その後、反応生成物を多量のヘキサンに滴下して反応生成物を凝固させた。さらに、この凝固物と同重量のテトラヒドロフランに再溶解し、多量のヘキサンで再度凝固させた。この再溶解一凝固操作を計3回行った後、得られた凝固物を40°Cで48時間真空乾燥し、目的とする共重合体A-1を得た。

【0049】クラッド層用共重合体(A)の調製例2

ドライアイス/メタノール還流器の付いたフラスコを窒素置換した後、重合開始剤として2, 2'-アゾビスジメチルバレロニトリルを0. 5 g、有機溶剤として乳酸エチルを54. 3 gを仕込み、重合開始剤が溶解するまで攪拌した。引き続いて、メタクリル酸4. 5 g、ジシクロペニタニルメタクリレート9. 0 g、メチルメタクリレート20. 4 g、およびn-ブチルアクリレート11. 3 gを仕込んだ後、緩やかに攪拌を始めた。その後、溶液の温度を80°Cに上昇させ、この温度で4時間重合を行った。その後、反応生成物を多量のヘキサンに滴下して反応生成物を凝固させた。さらに、この凝固物と同重量のテトラヒドロフランに再溶解し、多量のヘキサンで再度凝固させた。この再溶解一凝固操作を計3回行った後、得られた凝固物を40°Cで48時間真空乾燥し、目的とする共重合体A-2を得た。

【0050】コア部分用共重合体(A)の調製例3

ドライアイス/メタノール還流器の付いたフラスコを窒素置換した後、重合開始剤として2, 2'-アゾビスイソブチロニトリルを1. 3 g、有機溶剤として乳酸エチルを53. 8 gを仕込み、重合開始剤が溶解するまで攪拌した。引き続いて、メタクリル酸6. 7 g、イソボルニルメタクリレート15. 7 g、スチレン9. 0 g、およびn-ブチルアクリレート13. 5 gを仕込んだ後、緩やかに攪拌を始めた。その後、溶液の温度を80°Cに上昇させ、この温度で4時間重合を行った。その後、反応生成物を多量のヘキサンに滴下して反応生成物を凝固させた。さらに、この凝固物と同重量のテトラヒドロフ

ランに再溶解し、多量のヘキサンで再度凝固させた。この再溶解一凝固操作を計3回行った後、得られた凝固物を40°Cで48時間真空乾燥し、目的とする共重合体A-3を得た。

【0051】コア部分用共重合体(A)の調製例4(比較例)

ドライアイス/メタノール還流器の付いたフラスコを窒素置換した後、重合開始剤として2, 2'-アゾビスイソブチロニトリルを1. 3 g、有機溶剤として乳酸エチルを53. 8 gを仕込み、重合開始剤が溶解するまで攪拌した。引き続いて、ジシクロペニタニルメタクリレート17. 9 g、スチレン9. 1 g、およびn-ブチルアクリレート17. 9 gを仕込んだ後、緩やかに攪拌を始めた。その後、溶液の温度を80°Cに上昇させ、この温度で4時間重合を行った。その後、反応生成物を多量のヘキサンに滴下して反応生成物を凝固させた。さらに、この凝固物と同重量のテトラヒドロフランに再溶解し、多量のヘキサンで再度凝固させた。この再溶解一凝固操作を計3回行った後、得られた凝固物を40°Cで48時間真空乾燥し、目的とする共重合体A-4を得た。

【0052】クラッド層用共重合体(A)の調製例5(比較例)

ドライアイス/メタノール還流器の付いたフラスコを窒素置換した後、重合開始剤として2, 2'-アゾビスジメチルバレロニトリルを0. 5 g、有機溶剤として乳酸エチルを54. 3 gを仕込み、重合開始剤が溶解するまで攪拌した。引き続いて、メタクリル酸4. 5 g、メチルメタクリレート24. 9 g、およびn-ブチルアクリレート15. 8 gを仕込んだ後、緩やかに攪拌を始めた。その後、溶液の温度を80°Cに上昇させ、この温度で4時間重合を行った。その後、反応生成物を多量のヘキサンに滴下して反応生成物を凝固させた。さらに、この凝固物と同重量のテトラヒドロフランに再溶解し、多量のヘキサンで再度凝固させた。この再溶解一凝固操作を計3回行った後、得られた凝固物を40°Cで48時間真空乾燥し、目的とする共重合体A-5を得た。

【0053】放射線硬化性組成物J-1の調製

上述した共重合体A-1 32. 0重量部に対し、重合反応性組成物であるポリエステル多官能アクリレート(東亞合成製、M8100)を10. 0重量部、トリメチロールプロパントリアクリレートを6. 5重量部、放射線ラジカル重合開始剤であるIrgacure 369(チバスペシャリティ・ケミカルズ製)を3. 0重量部、乳酸エチルを48. 5重量部添加し、均一に混合することにより、放射線硬化性組成物J-1を得た。

【0054】放射線硬化性組成物J-2の調製

上述した共重合体A-2 27. 7重量部に対し、重合反応性組成物であるポリエステル多官能アクリレート(東亞合成製、M8100)を16. 6重量部、トリメチロールプロパントリアクリレートを11. 1重量部、

放射線ラジカル重合開始剤である Irgcure. 369 (チバスペシャリティ・ケミカルズ製) を 3.0 重量部、乳酸エチルを 41.6 重量部添加し、均一に混合することにより、放射線硬化性組成物 J-2を得た。

【0055】放射線硬化性組成物 J-3 の調製

上述した共重合体 A-3 35.0 重量部に対し、重合反応性組成物であるペンタエリスリトールトリアクリレートを 13.5 重量部、放射線ラジカル重合開始剤である Irgcure. 819 (チバスペシャリティ・ケミカルズ製) を 3.0 重量部、乳酸エチルを 48.5 重量部添加し、均一に混合することにより、放射線硬化性組成物 J-3を得た。

【0056】放射線硬化性組成物 J-4 の調製

上述した共重合体 A-1 32.0 重量部に対し、重合反応性組成物である多官能オキシラン化合物 (ダイセル化学工業製、エポリード GT 301) を 16.5 重量部、放射線カチオン重合開始剤である SP170 (旭電化製) を 3.0 重量部、乳酸エチルを 48.5 重量部添加し、均一に混合することにより、放射線硬化性組成物 J-4を得た。

【0057】放射線硬化性組成物 J-5 の調製

上述した共重合体 A-1 35.0 重量部に対し、重合反応性組成物であるジペンタエリスリトールヘキサアクリレート (日本化薬製、DPHA) を 13.5 重量部、放射線ラジカル重合開始剤である Irgcure. 369 (チバスペシャリティ・ケミカルズ製) を 3.0 重量部、乳酸エチルを 48.5 重量部添加し、均一に混合することにより、放射線硬化性組成物 J-5を得た。

【0058】放射線硬化性組成物 J-6 の調製 (比較例)

上述した共重合体 A-4 32.0 重量部に対し、重合反応性組成物であるポリエステル多官能アクリレート (東亞合成製、M8100) を 10.0 重量部、トリメチロールプロパントリアクリレートを 6.5 重量部、放射線ラジカル重合開始剤である Irgcure. 369 (チバスペシャリティ・ケミカルズ製) を 3.0 重量部、乳酸エチルを 48.5 重量部添加し、均一に混合することにより、放射線硬化性組成物 J-6を得た。

【0059】放射線硬化性組成物 J-7 の調製 (比較例)

上述した共重合体 A-5 27.7 重量部に対し、重合反応性組成物であるポリエステル多官能アクリレート (東亞合成製、M8100) を 16.6 重量部、トリメチロールプロパントリアクリレートを 11.1 重量部、放射線ラジカル重合開始剤である Irgcure. 369 (チバスペシャリティ・ケミカルズ製) を 3.0 重量部、乳酸エチルを 41.6 重量部添加し、均一に混合することにより、放射線硬化性組成物 J-7を得た。

【0060】 [実施例 1]

(1) 光導波路の形成

①下部クラッド層の形成

放射線硬化性組成物 J-2 をシリコン基板の表面上に、スピニコータで塗布し、ホットプレートを用いて 120°C、10 分間の条件でプリベークした。次いで、放射線硬化性組成物 J-2 からなる塗膜に、波長 365 nm、照度 20 mW/cm² の紫外線を 30 秒間照射して、放射線硬化させた。そして、この硬化膜を 200°C、1 時間の条件でポストベークをすることにより、厚さ 50 μm の下部クラッド層とした。

10 【0061】②コア部分の形成

次に、放射線硬化性組成物 J-1 を下部クラッド層の上にスピニコータで塗膜を形成し、ホットプレートを用いて 120°C、10 分の条件でブレーベークした。その後、放射線硬化性組成物 J-1 からなる厚さ 50 μm の塗膜に、幅 50 μm のライン状パターンを有するフォトマスクを介して、波長 365 nm、照度 20 mW/cm² の紫外線を 30 秒間照射して、塗膜を放射線硬化させた。次に、放射線照射した塗膜を 100°C、1 分間の条件で PEB を行った。次いで、放射線硬化させた塗膜を有する基板を 1.8% テトラメチルアンモニウムヒドロキシド水溶液 (TMAH) からなる現像液中に浸漬して、塗膜の未露光部を溶解させた。その後、200°C、1 時間の条件でポストベークを行い、幅 10 μm のライン状パターンを有するコア部分を形成した。

【0062】③上部クラッド層の形成

次いで、コア部分を有する下部クラッド層の上面に、放射線硬化性組成物 J-2 をスピニコータで塗布し、ホットプレートを用いて 120°C、10 分の条件でブリベークした。その後、放射線硬化性組成物 J-2 からなる塗膜に、波長 365 nm、照度 20 mW/cm² の紫外線を 30 秒間照射することにより、厚さ 50 μm の上部クラッド層を形成した。その後、この上部クラッド層を、200°C、6 時間の条件でポストベークした。

【0063】 [実施例 2~4、比較例 1~3] 下部クラッド層、コア部分、上部クラッド層を実施例 1 に記した組成物を用いる代わりに表 2 に示した組成物を用いる以外はすべて前記した手法と同じ手法により、光導波路を形成した。

【0064】(2) 光導波路形状の精度

上記した手法により設計したコア形状 (高さ 50 μm × ライン幅 50 μm) に関して、コア高さ、コア幅とともに 50 ± 5 μm の形状が形成された場合を「O」、それ以上、以下の形状になった場合を「X」とした。結果を表 2 に示す。

【0065】(3) 光導波路の伝送損失評価

このようにして得られた下部クラッド層、コア部分および上部クラッド層からなる光導波路について、波長 824 nm の光を一端から入射させた。そして、他端から出射する光量を測定することにより、単位長さ当たりの導波路損失をカットバック法により求めた。結果を表 2 に

示す。

【0066】

		J-1	J-2	J-3	J-4	J-5	J-6	J-7	J-8
(A)	A-1	32.0	-	-	32.0	35.0	-	-	32.0
	A-2	-	27.7	-	-	-	-	-	-
	A-3	-	-	35.0	-	-	-	-	-
(B)	M8100	10.0	16.6	-	-	-	10.0	16.6	-
	トリメチロ-アクリレート	6.5	11.1	-	-	-	6.5	11.1	-
	ベンタエリスリトールアクリレート	-	-	13.5	-	-	-	-	-
	エボリードG T 301	-	-	-	16.5	-	-	-	-
(C)	Irgcure 369	3.0	3.0	-	-	3.0	3.0	3.0	3.0
	Irgcure 819	-	-	3.0	-	-	-	-	-
	SP170	-	-	-	3.0	-	-	-	-
(D)	乳酸エチル	48.5	41.6	48.5	48.5	48.5	48.5	41.6	48.5
その他	A-4	-	-	-	-	-	32.0	-	-
	A-5	-	-	-	-	-	-	27.7	-
	イソブチリックアクリレート	-	-	-	-	-	-	-	16.5
合 計		100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

【0067】

【表2】

	実 施 例					比 較 例	
	1	2	3	4	5	1	2
光導波路構成							
下層クラッド層	J-2	J-2	J-2	J-2	J-7	J-7	J-7
コア部分	J-1	J-3	J-4	J-5	J-1	J-6	J-8
上層クラッド層	J-2	J-2	J-2	J-2	J-7	J-7	J-7
824 nmにおける コア・クラッド間の屈折率差 (Δn (%))	1.1	1.1	1.1	1.1	1.1	1.1	1.1
光導波路特性							
コア形状の精度	○	○	○	○	○	×	×
伝送損失 [dB/cm]	0.3	0.3	0.4	0.3	0.4	>1.0	>1.0

【0068】

【発明の効果】本発明の放射線硬化性組成物を使用することで、きわめて容易に、かつ短時間、高精度に光導波路を形成することができるようになった。また、本発明の放射線硬化性組成物で形成された光導波路は、低い伝送損失が得られることができた。このように、本発明の

光導波路の製造方法によれば、光導波路を効率的に製造することができるようになった。

【図面の簡単な説明】

【図1】本発明の光導波路の断面図である。

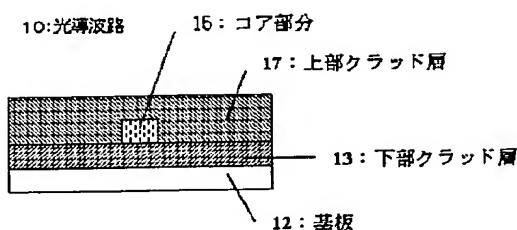
【図2】(a)～(e)は、光導波路の製造方法の一部工程図である。

【符号の説明】

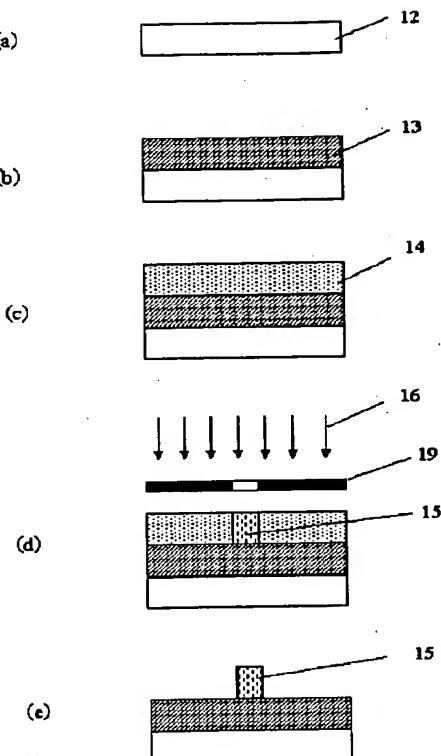
- 10 光導波路
12 基板
13 下部クラッド層
14 コア用薄膜

- 15 コア部分
16 放射線
17 上部クラッド層
18 リッジ
19 フォトマスク

【図1】



【図2】



フロントページの続き

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